

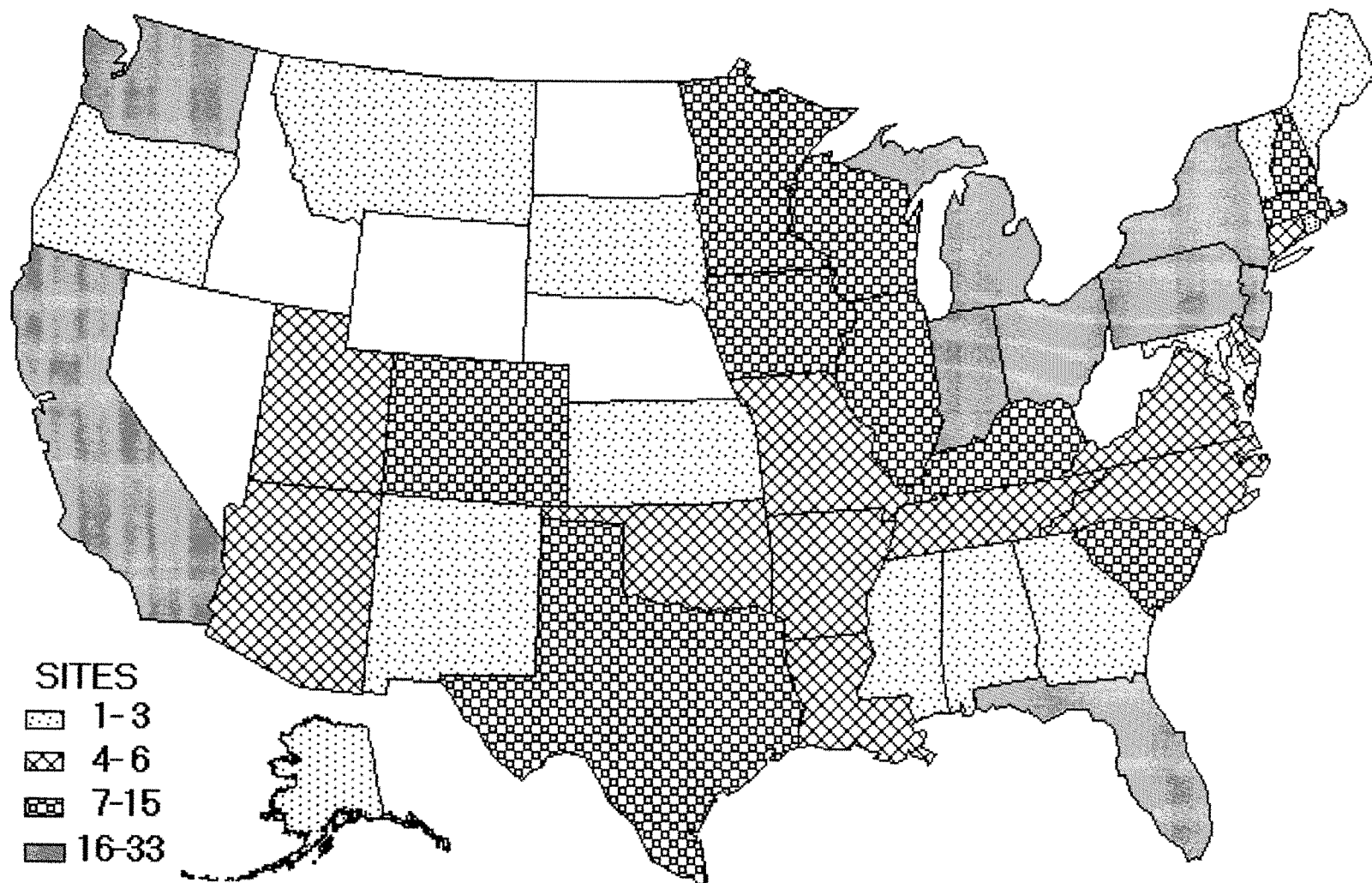
5. POTENTIAL FOR HUMAN EXPOSURE

5.1 OVERVIEW

Anthropogenic sources are responsible for much of the cyanide in the environment. Cyanide also occurs naturally in the fruits, seeds, roots, and leaves of numerous plants, and is released to the environment from natural biogenic processes from higher plants, bacteria, and fungi (Cicerone and Zellner 1983; Crutzen and Carmichael 1993; Fiksel et al. 1981; Knowles 1988). However, an estimate of the amount of cyanide released to the environment from natural biogenic processes is not available. The major cyanide releases to water are discharges from metal-finishing industries, iron and steel mills, and organic chemical industries (Fiksel et al. 1981). Effluents from the cyanidation process used in precious metal extraction contain high amounts of cyanide (Huiatt 1985; Scott 1985). The contribution of this source to the total cyanide discharge in water, however, is insignificant (Fiksel et al. 1981). Vehicle exhaust (Fiksel et al. 1981) and biomass burning (Crutzen and Carmichael 1993; Lobert and Warnatz 1993) are major sources of cyanide released into the air. The major sources of simple and complex cyanide releases to soil appear to be disposal of cyanide wastes in landfills and the use of cyanide-containing road salts (Fiksel et al. 1981; Gaffney et al. 1987). Cyanogen chloride is formed in drinking water from reaction of humic substances with chloramine produced during chlorination (Jacangelo et al. 1989; Ohya and Kanno 1987).

Thiocyanate is released to water primarily from discharges of industrial waste waters from coal processing and extraction of gold and silver (Boucabeille et al. 1994a). Thiocyanate is also found in mining waste waters where it results from the interaction of free cyanide with sulphur (Boucabeille et al. 1994b). Releases of thiocyanate to soil result from anthropogenic and natural sources. Anthropogenic releases occur primarily from direct application in herbicidal formulations and from disposal as byproducts from industrial processes. Nonanthropogenic sources include damaged or decaying tissues of plants from the family *Brassica* (e.g., cabbage, mustard, kale) (Brown and Morra 1993).

Cyanide (reported as cyanide, hydrogen cyanide, sodium cyanide, potassium cyanide, or copper(I) cyanide) has been identified in at least 406 of 1,428 current or former hazardous wastes sites that have been proposed for inclusion on the EPA National Priorities List (NPL) (HazDat 1996). However, the number of sites evaluated for cyanide is not known. The frequency of these sites within the United States can be seen in Figure 5- 1.

Figure 5-1. Frequency of NPL Sites with Cyanide Contamination

Derived from HazDat 1996

5. POTENTIAL FOR HUMAN EXPOSURE

Cyanide is released into air mainly as hydrogen cyanide gas and, to a lesser extent, as particulate cyanides. Hydrogen cyanide can potentially be transported over long distances before reacting with photochemically generated hydroxyl radicals. The residence time of hydrogen cyanide in the atmosphere has been estimated to be approximately 2.5 years, with a range of 1.3-5.0 years, depending on the hydroxyl radical concentration (Cicerone and Zellner 1983). Neither photolysis nor deposition by rainwater is expected to be a significant removal mechanism. Only 2% of the tropospheric hydrogen cyanide is expected to be transported to the stratosphere (Cicerone and Zellner 1983). In water, cyanide occurs most commonly as hydrogen cyanide. Hydrogen cyanide and soluble metal cyanides are expected to be removed from water primarily by volatilization. At low concentrations, some cyanide may also be removed by aerobic or anaerobic biodegradation (Callahan et al. 1979). At soil surfaces, volatilization of hydrogen cyanide is a significant loss mechanism for cyanides. In subsurface soil, cyanide at low concentrations would probably biodegrade under both aerobic and anaerobic conditions. In cases where cyanide levels are toxic to microorganisms (i.e., landfills, spills), water-soluble cyanides may leach into groundwater.

The environmental fate of thiocyanate has not been thoroughly investigated. Aerobic and anaerobic biodegradation are significant transformation processes for thiocyanates in water (Boucabeille et al. 1994a, 1994b; Shivaraman et al. 1985) and soil (Brown and Morra 1993). At near-ambient temperatures, sorption and volatilization are not significant partitioning processes for thiocyanate in soil (Brown and Morra 1993).

Despite the various ways cyanide is thought to be released into the environment, available monitoring data are limited. It appears that the general population is exposed to cyanide primarily by ingestion of foods that contain cyanides and, to a lesser extent, by consumption of contaminated drinking water and inhalation of contaminated air. Dermal absorption is not a significant exposure route for the general population. The concentration of cyanide in the northern hemisphere's non-urban troposphere ranges from 160 to 166 ppt (ppt = parts per trillion) (Cicerone and Zellner 1983; Jaramillo et al. 1989). The mean cyanide concentration in most surface waters is not greater than 3.5 µg/L (Fiksel et al. 1981). The cyanogen chloride concentration in drinking water is 0.45-0.80 µg/L (Krasner et al. 1989). The cyanide content in certain varieties of lima beans can be as high as 3 mg/g (Honig et al. 1983), although values between 0.10 and 0.17 mg/g are common in U.S. lima beans (Towill et al. 1978). Much lower cyanide concentrations in various cereal grains and cereal products have been reported, ranging from 0.001 to 0.45 µg/g (Honig et al. 1983). Mean cyanide concentrations in soybean products have been found to range from 0.07 to 0.3 µg/g; whereas, the mean cyanide concentration in soybean hulls was 1.24 µg/g (Honig et

5. POTENTIAL FOR HUMAN EXPOSURE

al. 1983). Due to the lack of data on cyanide content in total diet samples, the average daily intake could not be estimated.

Available monitoring data on thiocyanate are also very limited. No information was found in the available literature on major routes of exposure among the general population or on estimates of exposure. Because thiocyanate is a major metabolite of cyanide in the body, exposure to cyanide is a source of thiocyanate exposure. Thiocyanate occurs naturally in many edible plants. Vegetables in the family *Brassica* contain high levels of thiocyanate with concentrations ranging up to 660 µg/g, whereas other commonly consumed vegetables (e.g., spinach, radishes, celery) generally contain thiocyanates at concentrations <2 µg/g. Thiocyanate concentrations in milk and other dairy products and in meat have been reported to range from <1 to 9.0 µg/g and 0.5 to 0.7 µg/g, respectively (Weuffen et al. 1984). Thiocyanate concentrations in coal plant waste waters (Jensen and Tuan 1993) and mining waste waters (Boucabeille et al. 1994b) have been found to range from 100 to 1,500 mg/L and 300 to 450 mg/L, respectively. No data could be found in the available literature on thiocyanate concentrations in surface, ground, or drinking waters. Soils treated with rapeseed meal (from the family *Brassica*) contained thiocyanate at concentrations on the order of 6 µg/g (Brown et al. 1991).

It should be noted that the amounts of cyanide or thiocyanate found by chemical analysis are not necessarily the amounts that are bioavailable.

Among the general population, subpopulations with the most likely potential of exposure to cyanide at concentrations higher than background levels include active and passive tobacco smokers (Fiksel et al. 1981) and individuals who are exposed to house or other types of building fires (Andrews et al. 1989). Subpopulations with potential for exposure to cyanides or thiocyanates are residents who live near industrial sites releasing these compounds to the environment, residents who live near cyanide- or thiocyanate-containing hazardous waste sites, and people who consume foods, high in cyanogenic glycosides. Fetuses of smoking mothers or mothers exposed to high levels of environmental smoke may also be at risk of exposure to relatively high concentrations of cyanide and thiocyanate (Bottoms et al. 1982; EPA 1992f; Hauth et al. 1984).

Occupational exposures to cyanide occur primarily through inhalation and, less frequently, through dermal absorption. Estimates from the National Occupational Exposure Survey (NOES) conducted by the National Institute for Occupational Safety and Health (NIOSH) indicate that over 250,000 workers are potentially exposed to cyanide compounds, including cyanogen chloride and ammonium thiocyanate

5. POTENTIAL FOR HUMAN EXPOSURE

(NIOSH 1989a). Workers may be exposed to cyanides in various occupations, including electroplating, metallurgy, pesticide application, firefighting, steel manufacturing, gas works operations, and metal cleaning (Fiksel et al. 1981). The manufacture of industrial inorganic chemicals may be a potential source of occupational exposure to cyanogen chloride (NIOSH 1989a). Potential sources of occupational exposure to ammonium thiocyanate include the manufacture of electronic computing equipment, research and development laboratories, newspaper and other commercial printing, general medical and surgical hospitals, production of adhesives and sealants, and the construction and furniture industries (NIOSH 1989a). Potential occupational exposures may also occur during the direct application of herbicidal formulations (e.g., amitrol-T, a mixture of ammonium thiocyanate and amino-1,2,4-triazole) and from handling, treatment, or disposal of thiocyanate-containing wastes from industrial processes (Brown and Morra 1993).

5.2 RELEASES TO THE ENVIRONMENT

5.2.1 Air

Cyanide emissions into the air have been conservatively estimated at 44 million pounds a year based on data obtained during the mid-to-late 1970s. Over 90% of these emissions were attributed to releases from automobile exhaust. The second largest source of cyanide emission to the air was reported to be from the manufacture of methyl methacrylate, acrylonitrile, and hydrogen cyanide (Fiksel et al. 1981). More recent quantitative data regarding total cyanide emissions were not located in the available literature. Other smaller sources of cyanide release include emissions from iron and steel production, coal combustion (Fiksel et al. 1981), petroleum refineries (Fiksel et al. 1981), oil shale retorting processes (Hargis et al. 1986; Sklarew and Hayes 1984), municipal solid waste incinerators (Carotti and Kaiser 1972; Greim 1990), the combustion of acrylonitriles or other nitrogen-containing plastics (Brandt-Rauf et al. 1988; Fiksel et al. 1981), cigarette smoke (Baker and Proctor 1990; Fiksel et al. 1981; Guerin et al. 1987), volatilization from cyanide waste disposed of in landfills, and direct release to the atmosphere from certain agricultural pest control activities (Fiksel et al. 1981). In 1976, an estimated 137,000 pounds of cyanide was released in the air from agricultural pest control, 18,000-180,000 pounds from incineration, and 13,000-750,000 pounds from cigarette smoke (Fiksel et al. 1981). The production of coke or other coal carbonization processes also release hydrogen cyanide into the atmosphere (Cicerone and Zellner 1983). Hydrogen cyanide is also released into the atmosphere from natural biogenic processes from higher plants, bacteria, and fungi (Cicerone and Zellner 1983; Crutzen and Carmichael 1993; Fiksel et al. 1981; Knowles 1988). However, an estimate of the amount of hydrogen cyanide released from natural biogenic sources is

5. POTENTIAL FOR HUMAN EXPOSURE

not available (Cicerone and Zellner 1983). Crutzen and Carmichael (1993) have recently suggested that biomass burning represents an important source of atmospheric hydrogen cyanide. The combined worldwide emissions of hydrogen cyanide and acetonitrile due to biomass burning have been estimated to range from 0.5 to 1.7×10^{12} g of N/year (\approx 1.1- 3.7 billion pounds per year) (Crutzen and Andreae 1990). These estimates were based in part on highly uncertain global estimates of worldwide amounts of burned fuel and area and, consequently, have a high degree of uncertainty. Lobert and Warnatz (1993) have estimated that low molecular weight nitriles, primarily hydrogen cyanide and acetonitrile, represent about 4% of the nitrogen balance of biomass fires and contribute a major amount to their global atmospheric source.

The amount of hydrogen cyanide released to the atmosphere in 1993 by U.S. industrial facilities sorted by state is given in Table 5-1 (TR193 1995). According to TR193 (1995), an estimated total of 2.23 million pounds (approximately 1,010 metric tons) of hydrogen cyanide, amounting to approximately 73.1% of the total environmental release, was discharged to the air from manufacturing and processing facilities in the United States in 1993. The TRI data should be used with caution since only certain types of facilities are required to report. This is not an exhaustive list. No information is available in the TRI database for other cyanide and thiocyanate compounds in this profile because these compounds are not included under SARA, Title III, and therefore, are not among the chemicals that facilities are required to report (EPA 1993b).

Cyanides (reported as cyanide, hydrogen cyanide, sodium cyanide, potassium cyanide, calcium cyanide, or copper(I) cyanide) have been detected in air samples collected at 5 of the 406 hazardous waste sites where cyanides have been detected in some environmental medium (HazDat 1996). The HazDat information used includes data from both NPL and other Superfund sites. No information was found on detections of cyanogen, cyanogen chloride, or thiocyanates in air at any NPL or other Superfund hazardous waste sites (HazDat 1996).

5.2.2 Water

There are numerous sources that release cyanide into water. Cyanide is released into water from both point and nonpoint sources. The major point sources of cyanide released to water are discharges from publicly owned treatment works (POTWs), iron and steel production, and organic chemical industries (Fiksel et al. 1981). Estimates based on data from the mid-to-late 1970s indicate that these sources account for \approx 89% of the estimated 31 million pounds of total cyanide discharged annually to surface

Table 5-1. Releases to the Environment from Facilities That Manufacture or Process Hydrogen Cyanide

State ^a	City	Facility	Reported amounts released in pounds per year						
			Air	Water	Land	Underground injection	Total environment ^b	POTW transfer	Off-site waste transfer
AL	THEODORE	DEGUSSA CORP.	12,926				12,926		396
AL	THEODORE	VEBA CORP.	500				500	250	250
CA	SACRAMENTO	MITSUBISHI RAYON CO. LTD.	62,741				62,741		
CA	WILMINGTON	ULTRAMAR CORP.	30,500				30,500		
IL	CHICAGO	PMC INC.	10				10		
KY	ASHLAND	NA	5				5		
KY	ASHLAND	NA	10				10		
LA	FRANKLIN	CABOT CORP.	763,550				763,550		
LA	PLAQUEMINE	DOW CHEMICAL CO.	350				350		
LA	ST. GABRIEL	CIBA-GEIGY CORP.	327	136			463		11
LA	VILLE PLATTE	CABOT CORP.	589,750				589,750		
LA	WESTWEGO	NA	2,120				2,120		
MN	ROSEMOUNT	KOCH IND. INC.	120	260			380		
NH	NASHUA	HAMPSHIRE HOLDINGS CORP.	1,841				1,841		17
OH	LIMA	ARCADIAN CORP.	39,400				39,400		
OH	LIMA	HAMPSHIRE CHEMICAL CORP.	12				12		3
PA	WILLIAMSPORT	LONZA INC.	112				112	7	
SC	ORANGEBURG	ALBEMARLE CORP.	18,250				18,250		
SC	PIEDMONT	AMOCO CHEMICAL CO.	20,000				20,000	24	
SC	ROCK HILL	BASF CORP.	24,250				24,250		

5. POTENTIAL FOR HUMAN EXPOSURE

Table 5-1. Releases to the Environment from Facilities That Manufacture or Process Hydrogen Cyanide (continued)

State ^a	City	Facility	Reported amounts released in pounds per year						
			Air	Water	Land	Underground injection	Total environment ^b	POTW transfer	Off-site waste transfer
TN	MEMPHIS	E. I. DU PONT DE NEMOURS & CO.	45,734				45,734		
TN	MEMPHIS	ICI AMERICAS INC.	6,346				6,346		
TN	ROCKWOOD	AKZO NOBEL NV	12,560				12,560		
TX	ALVIN	MONSANTO CO.	10,700			170,000	180,700		
TX	BEAUMONT	E. I. DU PONT DE NEMOURS & CO.	9,530				9,530		
TX	DEER PARK	ROHM & HAAS CO.	203,203				203,203		
TX	DEER PARK	NA	280			1,268	1,548		
TX	DEER PARK	W. R. GRACE & CO.-CONN.							33
TX	FREEPORT	DOW CHEMICAL USA	11,026				11,026		
TX	HOUSTON	ISK ENTERPRISES CORP.	173				173		9
TX	NEDERLAND	ICI ACRYLICS INC.	1,450				1,450		2,050
TX	ORANGE	E. I. DU PONT DE NEMOURS & CO.	44,243			527,322	571,565		
TX	PAMPA	CABOT CORP.	152,586				152,586		
TX	PORT LAVACA	BP AMERICA	48,200				48,200		
TX	TEXAS CITY	NA	11,520				11,520		
TX	VICTORIA	E. I. DU PONT DE NEMOURS & CO.	10,782		12	123,225	134,019		41
UT	MAGNA	HERCULES INC.	52,978				52,978		

5. POTENTIAL FOR HUMAN EXPOSURE

Table 5-1. Releases to the Environment from Facilities That Manufacture or Process Hydrogen Cyanide (continued)

Reported amounts released in pounds per year									
State ^a	City	Facility	Air	Water	Land	Underground injection	Total environment ^b	POTW transfer	Off-site waste transfer
WI	SUPERIOR	MURPHY OIL USA INC.	44,192				44,192		
WV	WAVERLY	CABOT CORP.	1,634				1,634		
WY	GREEN RIVER	FMC CORP.	30				30		
Totals			2,233,941	396	12	821,815	3,056,164	281	2,810

Source: TRI93 1995

^a Post office state abbreviations used^b The sum of all releases of the chemical to air, land, water, and underground injection wells by a given facility

NA = not available; POTW = publicly owned treatment works

5. POTENTIAL FOR HUMAN EXPOSURE

waters. Since metal finishing and organic chemical industries are estimated to account for 90% of the influent to POTWs, they are the dominant sources of both direct and indirect discharge of cyanide to water (Fiksel et al. 1981). The amount of cyanide released to surface water and POTWs by U.S. industrial facilities that manufactured or processed cyanide compounds ranged from approximately 0 to 150,000 and 1,100 to 1,090,000 pounds, respectively (TR188 1990). These data indicate that the industrial discharge of cyanides into surface water and POTWs decreased substantially in 1988 in comparison to the estimated discharge during the 1970s. The amount of hydrogen cyanide released to surface water and POTWs in 1993 by U.S. industrial facilities sorted by state is shown in Table 5-1 (TR193 1995). According to TR193 (1995), estimated totals of 396 and 281 pounds of hydrogen cyanide were discharged to surface water and POTWs, respectively, in 1993. These combined releases amount to approximately 0.01% of the total environmental release of hydrogen cyanide. The TRI data should be used with caution since only certain facilities are required to report. This is not an exhaustive list. No information is available in the TRI database for other cyanide and thiocyanate compounds in this profile because these compounds are not included under SARA, Title III, and therefore, are not among the chemicals that facilities are required to report (EPA 1993g).

The effluents from the cyanidation process used in the extraction of precious metals from their ores may contain high levels of cyanide (Huiatt 1985; Scott 1985). The total cyanide content of typical tailing pond effluents from gold mill tailing ponds has been reported to range from 0.3 to 61 mg/L (Scott 1985). However, the contribution from this source to the total discharge of cyanide has been estimated to be negligible (Fiksel et al. 1981). Leachates from solid waste disposal sites are point sources of cyanide release to groundwater (Myers 1983; Venkataramani et al. 1984). No quantitative estimate of the amount of cyanide entering the groundwater from this point source was located. The nonpoint sources of cyanide released to water are comprised of agricultural and road runoff and atmospheric fallout and washout. The predominant sources of cyanides found in urban runoff samples were reported to be products of gasoline combustion and anticaking ingredients in road salts (Cole et al. 1984). It has been estimated that a maximum of ≈ 2 million pounds of sodium ferrocyanide that is used as an anticaking agent in road salts during the winter in the northeastern United States are washed off from roads into streams and storm sewers (Fiksel et al. 1981; Gaffney et al. 1987).

Cyanides (reported as cyanide, hydrogen cyanide, sodium cyanide, potassium cyanide, calcium cyanide, or copper(I) cyanide) have been detected in surface water samples at 117 of the 406 hazardous waste sites, in groundwater samples at 208 of the 406 hazardous waste sites, and in leachate samples at 43 of the

5. POTENTIAL FOR HUMAN EXPOSURE

406 hazardous waste sites where cyanides have been detected in some environmental medium (HazDat 1996). The HazDat information used includes data from both NPL and other Superfund sites.

Cyanogen chloride is formed in drinking water from the reaction of humic substances with chloramine formed during chlorination (Jacangelo et al. 1989; Ohya and Kanno 1987). In a mid-1970s EPA survey, cyanogen chloride was detected in drinking water from 8 of 10 U.S. cities (Fielding and Packham 1977). No information could be found in the available literature on the release of cyanogen to water. No information was found on detections of cyanogen or cyanogen chloride in surface or groundwater at any NPL or other Superfund hazardous waste sites (HazDat 1996).

Thiocyanate is released to water primarily from discharges of industrial waste waters from coal processing and extraction of gold and silver (Boucabeille et al. 1994a). Thiocyanate is also found in mining waste waters where it results from the reaction of free cyanide with sulphur (Boucabeille et al. 1994b). Thiocyanate has been detected in surface water samples at two of the eight hazardous waste sites, and in groundwater samples at five of the eight hazardous waste sites where thiocyanate has been detected in some environmental medium (HazDat 1996). The HazDat information used includes data from both NPL and other Superfund sites.

5.2.3 Soil

Estimates of amounts of cyanide released to soil from anthropogenic sources were not located. The largest anthropogenic sources of cyanide releases to soil probably result from the disposal of cyanide wastes in landfills and the use of cyanide-containing road salts (Fiksel et al. 1981; Gaffney et al. 1987). The amount of hydrogen cyanide released to land in 1993 by U.S. industrial facilities sorted by state is shown in Table 5-1 (TR193 1999). According to TR193 (1995), an estimated total of only 12 pounds of hydrogen cyanide, a negligible amount of the total environmental release, was discharged to land from U.S. manufacturing or processing facilities in 1993. However, some of the estimated 2,810 pounds of hydrogen cyanide wastes transferred off-site (see Table 5-1) may be ultimately disposed of in land. The TRI data should be used with caution since only certain facilities are required to report. This is not an exhaustive list. No information is available in the TRI database for other cyanide and thiocyanate compounds in this profile because these compounds are not included under SARA, Title III, and therefore, are not among the chemicals that facilities are required to report (EPA 19938).

5. POTENTIAL FOR HUMAN EXPOSURE

Natural biogenic processes of bacteria, fungi, and cyanogenic plants such as sorghum, soybeans, and cassava, also release cyanide into the soil (Knowles 1988; Towill et al. 1978; WHO 1992). Cyanides (reported as cyanide, hydrogen cyanide, sodium cyanide, potassium cyanide, calcium cyanide, or copper(I) cyanide) have been detected in soil samples at 187 of the 406 hazardous waste sites, in sediment samples at 97 of the 406 hazardous waste sites, and in soil gas samples at 1 of the 406 hazardous waste sites where cyanides have been detected in some environmental medium (HazDat 1996). The HazDat information used includes data from both NPL and other Superfund sites.

Cyanogen has been detected in soil samples at the one hazardous waste site where cyanogen has been found (HazDat 1996). Cyanogen chloride has been detected in soil samples at one of the two hazardous waste sites where this compound was detected in some medium (HazDat 1996). The HazDat information used includes data from both NPL and other Superfund sites. No other information could be found in the available literature on the release of cyanogen or cyanogen chloride to soil.

Releases of thiocyanate to soil result from anthropogenic and natural sources. Anthropogenic releases occur primarily from direct application in herbicidal formulations (e.g., amitrol-T, a mixture of ammonium thiocyanate and amino-1,2,4-triazole) and from disposal as byproducts from industrial processes.

Nonanthropogenic sources include damaged or decaying tissues of plants from the family Brassica (e.g., mustard, rape) (Brown and Morra 1993). Thiocyanate has been detected in soil samples collected at 2 of the 8 hazardous waste sites, and in sediment samples at 3 of the 8 hazardous waste sites where thiocyanate has been detected in some medium (HazDat 1996). The HazDat information used includes data from both NPL and other Superfund sites.

5.3 ENVIRONMENTAL FATE

5.3.1 Transport and Partitioning

Because hydrogen cyanide is a gas and has a relatively slow degradation rate in air (see Section 5.3.2), the atmosphere will be the ultimate sink for this compound. Almost all of the hydrogen cyanide released to the atmosphere remains in the lower altitudes (troposphere); only 2% of tropospheric hydrogen cyanide is transferred to the stratosphere (Cicerone and Zellner 1983). Cyanide has the potential to be transported over long distances from its emission source. Despite higher water solubility at saturated pressure, the removal of hydrogen cyanide by rainwater appears to be a negligible partitioning pathway (Cicerone and Zellner 1983). Because hydrogen cyanide is a gas, its removal from air by dry deposition is also likely to

5. POTENTIAL FOR HUMAN EXPOSURE

be negligible. However, metal cyanide particles, particularly water-soluble cyanide particles, are expected to be removed from the air by both wet and dry deposition.

Volatilization and sorption are the two physical processes that contribute to the loss of cyanide from water. At pH <9.2, most of the free cyanide in solution should exist as hydrogen cyanide, a volatile cyanide form (Towill et al. 1978). On the basis of Henry's law constant (see Table 3-2) and the volatility characteristics associated with various ranges of Henry's law constant (Thomas 1982), volatilization is a significant and probably dominant fate process for hydrogen cyanide in surface water (EPA 1992f). The most common alkali metal cyanides (e.g., sodium and potassium cyanide) may also be lost from surface water primarily through volatilization; whereas, the sparingly soluble metal cyanides such as copper (I) cyanide are removed from water predominantly by sedimentation and biodegradation (see Section 5.3.2.2) (EPA 1992f). Variations in the volatilization rate are expected because this process is affected by several parameters including temperature, pH, wind speed, and cyanide concentration (Callahan et al. 1979). Callahan et al. (1979) summarized the unpublished results of a laboratory study which indicated that the volatilization half-life of hydrogen cyanide from solutions at concentrations of 25-200 µg/L ranged from 22 to 110 hours. First order kinetics were observed. In outdoor experiments with moderate winds the rate of hydrogen cyanide loss increased by a factor of 2-2.5. In a study to evaluate the effect of cyanide on biochemical oxidation, there was a 50% loss of 6 ppm (mg/L) cyanide in river water kept in open biochemical oxygen demand bottles (without aeration) at pH 7.4 within ≈ 10 days (Ludzack et al. 1951). When the bottles were aerated (rate of aeration not given), 50% loss occurred in only ≈ 10 hours. The kinetics of the rate of loss due to volatilization were not rigorously investigated. The volatilization rate was pH-dependent, with the rate faster at a lower pH. Data indicated that volatilization is a more important fate process than cyanide loss due to chemical and biodegradation reactions (see Section 5.3.2.2) (Ludzack et al. 1951; Raef et al. 1977a). Because volatilization is not an important fate process for cyanide in groundwater, cyanide would be expected to persist for considerably longer periods of time in underground aquifers than in surface water.

Cyanides are sorbed by various natural media, including clays (Cruz et al. 1974), biological solids (Raef et al. 1977b), and sediments (Callahan et al. 1979). However, additional data are necessary to assess the significance of cyanide sorption to suspended solids and sediments in water. Hydrogen cyanide and the alkali metal cyanides are not likely to be strongly sorbed onto sediments and suspended solids because of their high water solubilities (see Table 3-2). Soluble metal cyanides may show somewhat stronger sorption than hydrogen cyanide, with the extent of sorption increasing with decreasing pH and increasing iron oxide, clay, and organic material contents of sediment and suspended solids (Callahan et al. 1979).

5. POTENTIAL FOR HUMAN EXPOSURE

However, sorption is probably insignificant even for metal cyanides when compared to volatilization and biodegradation (Callahan et al. 1979; EPA 1992f).

There are no data available to indicate that simple metal cyanides and hydrogen cyanide bioconcentrate in aquatic organisms (ASTER 1994; Callahan et al. 1979; EPA 1980a, 1985a, 1992f). Bioconcentration factors (BCFs) of 0.73 and 1.62 can be calculated for hydrogen cyanide, using the equation of Veith et al. (1979) for the BCF of a chemical in whole fish ($\log \text{BCF} = 0.85 \log K_{ow} - 0.70$) and the $\log K_{ow}$ values in Table 3-2. Similarly, the calculated BCF for sodium cyanide is 0.47. There is some evidence that metal cyanide complexes bioaccumulate in aquatic organisms. Fish from water with soluble silver and copper cyanide complexes were found to have metal cyanides in their tissues at concentrations ranging up to 168 and 304 $\mu\text{g/g}$, respectively (wet or dry weight not specified) (Callahan et al. 1979). However, the bioconcentration factors for such compounds in fish tissues are not known (ASTER 1994). It is difficult to evaluate the toxicologic significance of bioaccumulation of metal cyanide complexes because these compounds are much less toxic than soluble hydrogen cyanide, sodium cyanide, or potassium cyanide (EPA 1992f). There is no evidence of biomagnification of cyanides in the food chain (Towill et al. 1978). Volatilization of hydrogen cyanide would be a significant loss mechanism for cyanides from soil surfaces at a $\text{pH} < 9.2$. Cyanides are fairly mobile in soil. Mobility is lowest in soils with low pH and high concentrations of free iron oxides, positively charged particles, and clays (e.g., chlorite, kaolin, gibbsite), and highest in soils with high pH, high concentrations of free CaCO_3 and negatively charged particles, and low clay content (Callahan et al. 1979). Although cyanide has a low soil sorption capability, it is usually not detected in groundwater, probably because of fixation by trace metals through complexation or transformation by soil microorganisms (see Section 5.3.2.3) (Towill et al. 1978). In soils where cyanide levels are high enough to be toxic to microorganisms (i.e., landfills, spills), this compound may leach into groundwater (EPA 1984a). The possibility of cyanide leaching into groundwater under certain conditions is confirmed by the detection of cyanides in groundwater samples from solid waste sites (Anonymous 1990; Myers 1983; Venkataramani et al. 1984).

No information could be found in the available literature on the transport and partitioning of cyanogen or cyanogen chloride in the environment, or on their partitioning coefficients (K_{oc} K_{ow}) or Henry's law constants (see Table 3-2). Because these compounds are highly volatile gases (see Table 3-2), it would be expected that volatilization from water and soil would be a primary route of environmental partitioning. However, cyanogen is extremely reactive and does not persist in the environment unchanged (Towill et al. 1978).

5. POTENTIAL FOR HUMAN EXPOSURE

Similarly, little information could be found in the available literature on the environmental transport and partitioning of thiocyanate in the environment. At near ambient temperatures ($\approx 30\text{ }^{\circ}\text{C}$), it appears that sorption and volatilization are not significant partitioning processes for thiocyanate in soil, with thiocyanate losses due primarily to microbial degradation (see Section 5.3.2.3) (Brown and Morra 1993).

5.3.2 Transformation and Degradation

The various cyanide compounds included in this profile undergo a number of different transformation and degradation reactions in the environment as discussed in the following sections. The resulting environmental transformation products within different media are shown in Table 5-2.

5.3.2.1 Air

Most cyanide in the atmosphere exists almost entirely as hydrogen cyanide gas, although small amounts of metal cyanides may be present as particulate matter in the air (EPA 1984a). Hydrogen cyanide is very resistant to photolysis at wavelengths of normal sunlight (Callahan et al. 1978). The most important reaction of hydrogen cyanide in air is the reaction with photochemically generated hydroxyl radicals and subsequent rapid oxidation to carbon monoxide (CO) and nitric oxide (NO); photolysis and reaction with ozone are not important transformation processes, and reaction with singlet oxygen ($0\text{ }^1\text{D}$) is not a significant transformation process except at stratospheric altitudes where singlet oxygen is present in significant concentrations (Cicerone and Zellner 1983). The rate of hydroxyl radical reaction with hydrogen cyanide in the atmosphere depends on the altitude, and the rate of the reaction is at least an order of magnitude faster at lower tropospheric altitudes (0-8 km) than at upper tropospheric altitudes (10-12 km) (Cicerone and Zellner 1983). Based on a reaction rate constant of $3 \times 10^{-14}\text{ cm}^3/(\text{molecule}\cdot\text{sec})$ at $25\text{ }^{\circ}\text{C}$ (Fritz et al. 1982) and assuming an average hydroxyl radical concentration of $5 \times 10^5\text{ molecules/cm}^3$, the residence time for the reaction of hydrogen cyanide vapor with hydroxyl radicals in the atmosphere is ≈ 2 years. This value compares well with the atmospheric residence time derived by Cicerone and Zellner (1983) of approximately 2.5 years, with a range of 1.3-5.0 years, depending on the hydroxyl radical concentrations assumed. Using the equation $t_{1/2} = 0.693\tau$ for converting residence time (τ) to half-life ($t_{1/2}$) (Lyman 1982) and an estimated atmospheric residence time for hydrogen cyanide of 2-3 years, and assuming first-order kinetics for the reaction of hydrogen cyanide with hydroxyl radicals, an atmospheric half-life of 1.4-2.9 years can be calculated for hydrogen cyanide.

5. POTENTIAL FOR HUMAN EXPOSURE

Table 5-2. Environmental Transformation Products of Cyanide Compounds by Medium

Parent compound	Product(s)	Comments	Reference
Air			
HCN	HOCN + HO ₂ (unlikely) NO + CHO ⁻ (formed in minutes)	HNC·OH intermediate	Cicerone and Zellner 1983
	NO + CHO ⁻ (formed in minutes)	HCN·OH intermediate	Cicerone and Zellner 1983
Cyanogen	HCN, cyanic acid (NCOH), and other compounds	In the presence of water; slow reaction	Callahan et al. 1979
Water			
HCN	NH ₄ ⁺ + HCOO ⁻ in equilibrium with H ₂ NCHO + H ₂ NH ₄ ⁺ + HCOO ⁻	pH dependent (pH <1, t _{1/2} =10–1,000 h) Alkaline hydrolysis; very slow reaction	Callahan et al. 1979
CN ⁻	Metal cyanides	In the presence of excess metals; alkali metal cyanides very soluble; alkaline earth metal cyanides not very soluble	Callahan et al. 1979; EPA 1992f
	Complex metalocyanides	Excess CN ⁻ in the presence of metals; solubilities of metalocyanides vary	Callahan et al. 1979; EPA 1992f
CN ⁻	>99% HCN	pH<7	Towill et al. 1978
	NH ₃ + CO ₂ (NH ₃ converted to nitrite and nitrate in presence of nitrifying bacteria)	Aerobic biotransformation	Richards and Shieh 1989
	N ₂ + CO ₂	Anaerobic biotransformation under denitrification conditions	Richards and Shieh 1989
HCN/CN ⁻ salts	Thiocyanate (SCN ⁻), NH ₃ + CO ₂ , CHOO ⁻	Biotransformation	Towill et al. 1978
Cyanogen	HCN, cyanic acid (NCOH), and other compounds	Slow reaction	Callahan et al. 1979
Metalocyanides	CN ⁻ (possibly)	Photolysis	Callahan et al. 1979
	Isocyanate (OCN ⁻)	Oxidation	EPA 1992f
	CO ₂ + N ₂	In the presence of strong oxidizing agents	EPA 1992f
SCN ⁻	HCN	In acidic media	Callahan et al. 1979

5. POTENTIAL FOR HUMAN EXPOSURE

Table 5-2. Environmental Transformation Products of Cyanide Compounds by Medium (continued)

Parent compound	Product(s)	Comments	Reference
Sediment and Soil			
CN ⁻	Metallocomplexes	Abiotic transformation in the presence of metals	Towill et al. 1978
	NH ₃ + CO ₂ (NH ₃ converted to nitrite and nitrate in presence of nitrifying bacteria)	Aerobic biotransformation (predicted from fate in wastewater)	Richards and Shieh 1989
	N ₂ + CO ₂	Aerobic biotransformation under denitrification conditions (predicted from fate in wastewater)	Richards and Shieh 1989
SCN ⁻	COS (possibly; microbial degradation pathway not known)	Microbial degradation	Brown and Morra 1993
Wastewater/Sludge			
CN ⁻	NH ₃ + CO ₂ (NH ₃ converted to nitrite and nitrate in presence of nitrifying bacteria)	Aerobic biotransformation	Richards and Shieh 1989
	N ₂ + CO ₂	Anaerobic biotransformation under denitrification conditions	Richards and Shieh 1989
CN ⁻ /metallo-cyanides (including cuprocyanide)	NH ₃ + CO ₂	Microbial degradation in mining wastewaters	Boucabeille et al. 1994b
SCN ⁻	NH ₃ + CO ₂ + SO ₄ ⁼	Microbial degradation in mining wastewaters	Boucabeille et al. 1994a
	COS + NH ₃	Microbial degradation in activated sludge	Katayama et al. 1993

h = hours

5. POTENTIAL FOR HUMAN EXPOSURE

Cyanogen is extremely reactive and does not persist in the environment unchanged (Towill et al. 1978). However, no specific information was found in the available literature on the transformation and degradation of cyanogen, or cyanogen chloride, in air. Cyanogen does react slowly with water to yield hydrogen cyanide and cyanic acid (HOCN) among other products (Callahan et al. 1979) and this hydrolysis reaction may be a possible atmospheric degradation pathway.

No information was found in the available literature on the transformation and degradation of thiocyanates in air.

5.3.2.2 Water

Cyanide occurs most commonly as hydrogen cyanide in water, although it can also occur as the cyanide ion, alkali and alkaline earth metal cyanides (potassium cyanide, sodium cyanide, calcium cyanide), relatively stable metalocyanide complexes (ferricyanide complex $[\text{Fe}(\text{CN})_6]^{3-}$), moderately stable metalocyanide complexes (complex nickel and copper cyanide), or easily decomposable metalocyanide complexes (zinc cyanide $[\text{Zn}(\text{CN})_2]$, cadmium cyanide $[\text{Cd}(\text{CN})_2]$). Hydrogen cyanide and cyanide ion combined are commonly termed free cyanide. The environmental fate of these cyanide compounds varies widely (Callahan et al. 1979).

Oxidation, hydrolysis, and photolysis are the three predominant chemical processes that may cause loss of simple cyanides in aquatic media. Cyanides are oxidized to isocyanates by strong oxidizing agents; the isocyanates may be further hydrolyzed to ammonia and carbon dioxide (Towill et al. 1978). However, it has not yet been determined whether such oxidation and subsequent hydrolysis of isocyanate is a significant fate process in natural waters known to contain peroxy radicals (EPA 1992f).

In water, hydrogen cyanide and cyanide ion exist in equilibrium with their relative concentrations primarily dependent on pH and temperature. At pH <8, >93% of the free cyanide in water will exist as undissociated hydrogen cyanide (Towill et al. 1978). Hydrogen cyanide is hydrolyzed to formamide which is subsequently hydrolyzed to ammonium and formate ions (Callahan et al. 1979). However, the relatively slow rates of hydrolysis reported for hydrogen cyanide in acidic solution (Kreible and McNally 1929; Kreible and Peiker 1933) and of cyanides under alkaline conditions (Wiegand and Tremelling 1972) indicate that hydrolysis is not competitive with volatilization and biodegradation for removal of free cyanide from ambient waters (Callahan et al. 1979).

5. POTENTIAL FOR HUMAN EXPOSURE

The alkali metal cyanides are very soluble in water. As a result, they readily dissociate into their respective anions and cations when released into water. Depending on the pH of the water, the resulting cyanide ion may then form hydrogen cyanide or react with various metals in natural water. The proportion of hydrogen cyanide formed from soluble cyanides increases as the water pH decreases. At pH <7, >99% of the cyanide ions in water is converted to hydrogen cyanide (Towill et al. 1978). As the pH increases, cyanide ions in the water may form complex metalocyanides in the presence of excess cyanides; however, if metals are prevalent, simple metal cyanides are formed. Unlike water-soluble alkali metal cyanides, insoluble metal cyanides such as are not expected to degrade to hydrogen cyanide (Callahan et al. 1979).

The significance of photolysis in the fate of cyanides in water has not been fully investigated. Hydrogen cyanide and cyanide ions in aqueous solution have been found to be very resistant to photolysis by natural sunlight, except under heterogeneous photocatalytic conditions (Callahan et al. 1979; Frank and Bard 1977). Photocatalytic oxidation may not be significant in natural waters, however, because of significant light reduction at increasingly greater depths (EPA 1992f). In clear water or at water surfaces, some metalocyanides, such as ferrocyanides and ferricyanides, may decompose to the cyanide ion by photodissociation and subsequently form hydrogen cyanide. Because of adsorption of ferrocyanide onto soil surfaces and sediment of surface waters, and light scattering in turbid waters in the field, the rate of free cyanide formation from the photolysis of ferrocyanide in runoff and surface water from wash out of ferrocyanide in de-icing salt will be slower than from laboratory photolysis with clean water (Callahan et al. 1979).

Biodegradation is an important transformation process for cyanide in natural surface waters, and is dependent on such factors as cyanide concentrations, pH, temperature, availability of nutrients, and acclimation of microbes. However, additional data are needed to assess the relative significance of this process in determining the fate of aquatic cyanides (Callahan et al. 1979). Although cyanide is toxic to microorganisms at concentrations as low as 5-10 mg/L (Klecka et al. 1985; Malaney et al. 1959), acclimation increases tolerance to this compound (Raef et al. 1977a). A number of pure cultures of microorganisms degrade low concentrations of cyanide under both aerobic and anaerobic conditions (Callahan et al. 1979; EPA 1992f; Towill et al. 1978). However, biodegradation data derived from use of a pure culture are not strictly relevant to natural waters which contain mixed cultures. Mixed microorganisms in sewage sludge or activated sludge acclimated to cyanide also significantly biodegrade concentrations ≤ 100 mg/L of most simple and complex cyanides (Gaudy et al. 1982; Pettet and Mills 1954; Richards and Shieh 1989; Shivaraman et al. 1985). In a study to evaluate the effect of cyanide on biochemical oxidation conducted in sealed vessels, a 50% loss of cyanide at concentrations ≤ 6 mg/L in

5. POTENTIAL FOR HUMAN EXPOSURE

2 natural river waters occurred at times estimated to range from <10 to 24 days (Ludzack et al. 1951). The rate of loss appeared to be linear with time. These data may represent a biodegradation half-life; however, the possibility of loss by chemical reaction was not addressed in this study.

Most of the available information on the mechanisms of biodegradation of cyanides in water comes from studies to evaluate this process as a means of detoxication of cyanide-containing wastes. Raybuck (1992) has recently reviewed the role of microbes in cyanide degradation and has categorized the microbial enzymes which use cyanide as a substrate according to the following types of reactions: substitution/addition, hydrolysis, oxidation, and reduction. Sulfur transferases such as rhodanese are involved in substitution reactions which result in the conversion of cyanide to the less toxic thiocyanate; whereas, pyridoxal phosphate enzymes are involved in substitution/addition reactions which result in production of nitrile derivatives of α -amino acids. These organic nitriles may then be ultimately degraded via enzyme catalyzed hydrolysis to either the corresponding amino acid and ammonia (without formation of the free amide), or to the carboxylic acid and ammonia (via formation of the free amide). The cyanide hydratase and cyanidase enzymes catalyze the hydrolysis of cyanide to formamide or formic acid and ammonia, respectively. A strain of *Alcaligenes xylosoxidans subsp. denitrificans* has been found to effectively hydrolyze cyanide concentrations up to 300 mg/L down to very low levels (0.01-0.02 mg/L) and to be resistant to inactivation by chloride, sulfate, iodide, Fe^{+2} , Zn^{+2} , or Ni^{+2} at concentrations of 70 mg/L (Basheer et al. 1992). Thus, these hydrolytic systems are some of the most promising for detoxification of cyanide containing waste waters (Raybuck 1992). Few microbial systems have been identified that are capable of direct oxidation or reduction of cyanide. *Bacillus pumilus*, *Pseudomonas fluorescens*, and *Pseudomonas paucimobili* have all been found to oxidize cyanide to ammonia and carbon dioxide (Meyers et al. 1993). Cyanic acid has been postulated to be an intermediate in the aerobic oxidation of cyanide by *P. jhorensens*. In an aerobic batch bioreactor experiment, *Pseudomonas putida* was found to significantly degrade 4 mM sodium cyanide (cyanide concentration approximately 100 mg/L) to ammonia and carbon dioxide (Chapatwala et al. 1993). Other evidence indicates that formamide and formate are additional transformation products in microbial oxidation of cyanide by this species, inferring that there may be more than one pathway of cyanide biotransformation involved (Kunz et al. 1992; White et al. 1988). Several bacterial species have been identified recently that are capable of oxidative degradation of metalocyanides (Silva-Avalos et al. 1990). The cyanide oxygenase system involved in this process offers a new technology for the treatment of metal cyanide wastes (Raybuck 1992).

5. POTENTIAL FOR HUMAN EXPOSURE

The ferrocyanide complex is not easily biodegradable (Belly and Goodhue 1976; Pettet and Mills 1954). However, when an aqueous solution of potassium ferrocyanide was seeded with pure culture of *Pseudomona aeruginosa*, *E. coli*, or a mixture of the two bacteria, formation of free cyanide was observed after a delay period of ≈ 2 days (Cherryholmes et al. 1985). The rate of free cyanide formation increased with addition of nutrient in water, and a free cyanide concentration $\leq 4,000 \mu\text{g/L}$ was detected at the end of 25 days. It was shown that the free cyanide formation was due to biodegradation and not to either photolysis or hydrolysis. The relevance of this study to the fate of ferrocyanide complexes in natural water or industrial effluents is difficult to assess because cyanide concentrations used in these experiments (3,300 mg/L) are rarely encountered in these media.

Biodegradation is also a significant transformation process for thiocyanates in natural waters; however, additional data are needed to assess the relative importance of this process. Like cyanide, thiocyanate is toxic to microorganisms at high concentrations and acclimated cultures have increased tolerance to this compound (Boucabeille et al. 1994a). Laboratory studies have shown that at concentrations up to at least 1.42 g/L, thiocyanate was completely degraded within 4 days to ammonia and sulfate ion ($\text{SO}_4^{=}$) by an acclimatized co-culture of two bacteria (*Acinetobacter johnsonii* and *Pseudomonas diminuta*) isolated from sludge from an urban sewage treatment plant (Boucabeille et al. 1994a). Thiosulfate ion ($\text{S}_2\text{O}_3^{=}$) was identified as the intermediate in this degradation pathway.

Several studies document the biodegradation of mixtures of cyanides and thiocyanate in waste waters (e.g., Boucabeille et al. 1994b; Mudder and Whitlock 1984; Paruchuri et al. 1990; Shivaraman et al. 1985). Under aerobic conditions, the biodegradation of cyanides and thiocyanate initially produces ammonia, which is converted to nitrite and nitrate in the presence of nitrifying bacteria; whereas anaerobic biodegradation under denitrification conditions may produce nitrogen (Richards and Shieh 1989). Complete biodegradation of simple and metal complexed cyanides and thiocyanate from mining waste waters by various *Pseudomonas*, *Vibrionacas*, and *Enterobacterias* has recently been reported (Boucabeille et al. 1994b). Biodegradation of cyanide and thiocyanate resulted in the formation of ammonia, with or without accumulation of nitrite and/or nitrate, depending on whether a batch, fed-batch, or continuous treatment process was used. Sulphate ions were produced from thiocyanate degradation. Shivaraman et al. (1985) reported the uninhibited microbial degradation of thiocyanate and cyanide to ammonia by acclimatized mixed cultures at cyanide concentrations up to $22.40 \pm 1.34 \text{ mg/L}$; whereas, Paruchuri et al. (1990) have reported the complete inhibition of microbial degradation of thiocyanate in the presence of 10 mg/L cyanide.

5. POTENTIAL FOR HUMAN EXPOSURE

Cyanogen reacts slowly with water to produce hydrogen cyanide, cyanic acid, and other compounds (Callahan et al. 1979). No information could be found in the available literature on the transformation of cyanogen chloride in water; however, volatilization would be expected to be the predominant fate process for both cyanogen chloride and cyanogen in water.

5.3.2.3 Sediment and Soil

Analogous to the fate of cyanides in water, it is predicted that the fate of cyanides in soil would be dependent on cyanide concentrations, pH, temperature, metal content, concentration of microbes, availability of nutrients, and acclimation of microbes. Cyanide may occur as hydrogen cyanide, alkali metal salts, or as immobile metalocyanide complexes. In soil, cyanide present at low concentrations would biodegrade under aerobic conditions with the initial formation of ammonia, which will be converted to nitrite and nitrate in the presence of nitrifying bacteria. Under anaerobic conditions, cyanides will denitrify to gaseous nitrogen (Richards and Shieh 1989). Upper limits of 200 and 2 ppm (mg/kg CN⁻), respectively, have been reported for uninhibited aerobic and anaerobic biodegradation of cyanide in soil (Fueller 1984); however, these limits have not been confirmed in other studies (Thomas and Lester 1993). Cyanide ions in soil are not involved in oxidation-reduction reactions but may undergo complexation reactions with metal ions in soil (Towill et al. 1978).

No information could be found in the available literature on the transformation of cyanogen or cyanogen chloride in soil or sediment; however, because these compounds are highly volatile gases, biotic or abiotic degradation would not be expected to be significant fate processes compared to volatilization.

The fate of thiocyanate in soil is largely uncharacterized. Early studies have shown that thiocyanate can undergo both aerobic (Betts et al. 1979) and anaerobic microbial degradation (Betts et al. 1979; Stafford and Calley 1969; Youatt 1954); however, the degradation pathway has not been defined (Brown and Morra 1993). Saturated soils treated with thiocyanate were found to emit carbonyl sulfide (COS) (Minami 1982; Minami and Fukushi 1981). Katayama et al. (1992, 1993) have reported the formation of carbonyl sulfide from the biodegradation of thiocyanate by pure and mixed cultures of *Thiobacillus thioparus*. These species are ubiquitous in soil (Kelly and Harrison 1989). In a recent laboratory investigation of the fate of ionic thiocyanate in six different soils, Brown and Morra (1993) concluded that microbial degradation is the primary mechanism for thiocyanate disappearance at or below 30 °C, with carbonyl sulfide proposed as a possible hydrolysis product. Loss of thiocyanate at higher temperatures (50-60 °C) did not appear to result from microbial degradation; the observed decreases in thiocyanate concentrations

5. POTENTIAL FOR HUMAN EXPOSURE

of soil extracts with incubation time at elevated temperatures were postulated to result primarily from increased sorption or increased sorption kinetics, but abiotic catalysis of thiocyanate degradation was also noted as a possible cause.

5.4 LEVELS MONITORED OR ESTIMATED IN THE ENVIRONMENT

The values reported for environmental levels of cyanide and thiocyanate must be interpreted with caution. Methods for the analysis of cyanide and thiocyanate have many interferences. In addition, samples containing cyanide and/or thiocyanate may not be stable if the samples are not carefully preserved. It should be noted that the amounts of cyanide or thiocyanate found by chemical analysis are not necessarily the amounts that are bioavailable.

Reliable evaluation of the potential for human exposure to cyanide depends in part on the reliability of supporting analytical data from environmental samples and biological specimens. In reviewing data on cyanide levels monitored in the environment, it should also be noted that the amount of chemical identified analytically is not necessarily equivalent to the amount that is bioavailable.

5.4.1 Air

The concentration of hydrogen cyanide in the northern hemisphere's non-urban troposphere ranges from 160 to 166 ppt (Cicerone and Zellner 1983; Jaramillo et al. 1989). Although ambient monitoring data regarding cyanide in air near source areas (e.g., hydrogen cyanide manufacturing industries, coke production industries, waste disposal sites) were not located in the available literature, the hydrogen cyanide concentration in the vicinity of the source areas would be expected to be higher than the nonurban tropospheric concentration. The semiquantitatively measured hydrogen cyanide concentrations in the offgas from shale oil retorting processes ranged from 6 to 39 ppm in one retort at one site; however, hydrogen cyanide was not detected in retorts at another site (Sklarew and Hayes 1984).

No information could be found in the available literature on concentrations of cyanogen, cyanogen chloride, or thiocyanates in air.

5. POTENTIAL FOR HUMAN EXPOSURE

5.4.2 Water

Cyanide has been detected in waste waters from plating industries at concentrations up to 100,000 mg/L (Chen et al. 1994; Grosse 1986); from a textile industry at a maximum concentration of 0.2 mg/L (Rawlings and Samfield 1979); in the primary and secondary effluents from a Los Angeles City waste water treatment plant at mean concentrations of 29 ± 4 and 10 ± 6 µg/L (0.03 and 0.01 mg/L), respectively (Young 1978); and in the final effluent from a Los Angeles County waste water treatment plant at a mean concentration of 240 µg/L (0.24 mg/L) (Young 1978). Waste waters from a mining site storage basin were found to contain cyanide at concentrations of >10 mg/L as simple cyanides; 20-80 mg/L as combined simple cyanides and copper(I) cyanide; 20-190 mg/L as combined simple cyanides, copper(I) cyanide, and ferrocyanide; and 300-450 mg/L as thiocyanate (Boucabeille et al. 1994b). Waste waters from gold mines have been reported to contain total cyanide and thiocyanate concentrations ranging from 0.5 to 10 mg/L and 45 to 75 mg/L, respectively (Mudder and Whitlock 1984). Weak acid dissociable (WAD) cyanide was measured in tailing ponds at several Nevada gold mines in 1990; the concentrations ranged from 8.4 to 216 mg/L at the discharge pipe and from 7.8 to 11.3 mg/L at the reclaim area (Henny et al. 1994). In New York state alone, 47 industries discharged 3,877 pounds of cyanide into streams in 1982 (Rohmann et al. 1985). Cyanide has also been found in groundwater below landfills and disposal sites (Anonymous 1990; Myers 1983; Venkataramani et al. 1984). A maximum cyanide concentration of 1,200 µg/L (1.2 mg/L) was found in shallow groundwater ≤ 3 meters below an inactive drum recycling facility in Miami, Florida (Myers 1983). Cyanide concentrations were found to range from 0.005 to 14.0 mg/L in the leachates from 14 of 43 U.S. landfills with industrial wastes; the “typical” cyanide concentration was reported to be 0.008 mg/L (Venkataramani et al. 1984). Data from the Nationwide Urban Runoff Program as of 1982 indicate that cyanide was found in urban runoff samples collected in 4 of 15 urban areas across the United States: Denver, Colorado; Long Island, New York; Austin Texas; and Bellevue, Washington. Overall, cyanide was detected in 16% of the urban runoff samples collected, at concentrations ranging from 2 to 33 µg/L (Cole et al. 1984).

Based on data obtained from the EPA STORET database, the mean cyanide concentration in most surface waters tested in the United States is not >3.5 µg/L (Fiksel et al. 1981); however, 37 of 50 states (74%) have locales where cyanide concentrations in ambient water are >3.5 µg/L. Areas with levels >200 µg/L include portions of southern California, North Dakota, South Dakota, Iowa, northwest Georgia, western New York, and western Pennsylvania (Fiksel et al. 1981). It should be noted that these results are applicable only to the period from the late 1970s to the early 1980s. Furthermore, the reliability of some of these early STORET data may be questionable. Analyses of more recent STORET cyanide data could not be found.

5. POTENTIAL FOR HUMAN EXPOSURE

Cyanide at a concentration $>1 \mu\text{g/L}$ was detected in water from the Great Lakes (Great Lakes Water Quality Board 1983). The concentration of cyanide in 104 samples collected during 1980 and 1981 at various points on the Ohio River and its tributaries was reported to range from <5 to $80 \mu\text{g/L}$ (Ohio River Valley Sanitation Commission 1982). The highest concentration was detected in water from Beaver Falls, Pennsylvania.

Cyanogen chloride is formed in drinking water due to reaction of humic substances with chloramine formed during chlorination (Ohya and Kanno 1987). It has been reported that the concentration of cyanogen chloride in drinking water is most influenced by the final disinfectant. The use of chloramine as a final disinfectant produces levels of cyanogen chloride that are 4-15 times higher than levels produced when chlorine is used (Jacangelo et al. 1989; Krasner et al. 1989). Cyanogen chloride was qualitatively detected during a 1975 survey of Cincinnati, Ohio drinking water (Kopfler et al. 1977). A lo-city survey that was conducted as part of the 1974 EPA National Organics Reconnaissance Survey revealed that cyanogen chloride was present in 8 of 10 drinking water supplies analyzed (no quantitative concentration values given) (Bedding et al. 1982). In a 1988 survey of 35 water utilities, the quarterly median cyanogen chloride concentrations in drinking water ranged from 0.45 to $0.80 \mu\text{g/L}$ (Krasner et al. 1989).

No information could be found in the available literature on the levels of thiocyanate in ground, surface, or drinking water. Thiocyanate is found in concentrations ranging from 100 to $1,500 \text{ mg/L}$ in coal plant waste waters (Ganczarzyk 1979; Jensen and Tuan 1993), and from 300 to 450 mg/L in mining (gold extraction) waste waters (Boucabeille et al. 1994b).

5.4.3 Sediment and Soil

No information could be found in the available literature on concentrations of cyanides, cyanogen, or cyanogen chloride in soil or sediments. The highly volatile gases hydrogen cyanide, cyanogen, and cyanogen chloride (see Table 3-2) would not be expected to be present in sediment or soil in any appreciable amounts.

Monitoring data on thiocyanate concentrations in soils are scarce. Concentrations of thiocyanate in soils amended with defatted seed meal of *Brassica napus L.* (rapeseed) were reported to be on the order of $6 \mu\text{g/g}$ (Brown et al. 1991). No information could be found in the available literature on thiocyanate concentrations in sediments.

5. POTENTIAL FOR HUMAN EXPOSURE

5.4.4 Other Environmental Media

The primary cyanide source in food is cyanogenic glycosides. Plants containing cyanogenic glycosides can produce hydrogen cyanide by acid hydrolysis or by the action of the enzyme β -glucosidase (EPA 1980a; Fiksel et al. 1981; Seigler 1991). Hydrogen cyanide release can occur either during maceration, which activates the intracellular β -glucosidase, or in the gut by the action of β -glucosidase produced by microflora. The level of activity of β -glucosidase in the gut depends on the bacterial composition and the pH level (WHO 1992). There are approximately 60 known cyanogenic glycosides, all of which differ considerably in bioavailability (Seigler 1991). Those cyanogenic glycosides that are absorbed intact from the gut are not metabolized to hydrogen cyanide by mammalian enzymes. The potential toxicity of cyanogenic plants depends on their ability to release hydrogen cyanide during preparation or digestion at concentrations high enough to be of concern for human health (WHO 1992).

Over 2,650 plant species can produce hydrogen cyanide (Seigler 1991; Swain et al. 1992). These include edible plants such as almonds, pits from stone fruits (e.g., apricots, peaches, plums, cherries), sorghum, cassava, soybeans, spinach, lima beans, sweet potatoes, maize, millet, sugarcane, and bamboo shoots (Fiksel et al. 1981). The cyanogenic glycoside content of a foodstuff is usually expressed as the amount of cyanide released by acid hydrolysis; glycoside concentrations are rarely reported (WHO 1992).

Cyanide levels measured in some foods are as follows: cereal grains and their products, 0.001-0.45 $\mu\text{g/g}$; soy protein products, 0.07-0.3 $\mu\text{g/g}$; and lima beans, 0.1-3 mg/g (Honig et al. 1983; Towill et al. 1978). The cyanide equivalent of total cyanogenic content (i.e., cyanogenic glycosides, cyanohydrins, and hydrogen cyanide) of cassava root has been reported to range from 91 to 1,515 mg/kg hydrogen cyanide (86-1,458 $\mu\text{g/g CN}^-$) dry weight (d/w) (O'Brien et al. 1992). Cassava is the major starchy food for more than 300 million people in many tropical countries of the world, and many cultivars are toxic (Seigler 1991). Effective processing can reduce the amount of total cyanogens in fresh cassava roots to significantly lower levels in foods ready for consumption (Mlingi et al. 1993; O'Brien et al. 1992). For example, the mean cyanide content in garri (a flour product of grated, pressed, and fermented cassava root pulp) from a city market in Nigeria ranged from 10.6 to 22.1 $\mu\text{g/g d/w}$ (Ukhun and Dibia 1989). A somewhat wider distribution of results was obtained in another recent evaluation of commercial garri from three main garri-producing Nigerian communities (Aletor 1993). The mean total cyanide content (glucosidic plus non-glucosidic) of 38.8% of all samples ($n = 108$) ranged from 0 to 10 mg/kg hydrogen cyanide (0-9.6 $\mu\text{g/g CN}^-$); whereas, 40.7, 12.9, and 7.4% of the samples had mean total cyanide contents of 10-20, 20-30, and 30-40 mg/kg hydrogen cyanide (9.6-19, 19-29, and 29-39 $\mu\text{g/g CN}^-$), respectively.

5. POTENTIAL FOR HUMAN EXPOSURE

The mean cyanide content of domestic samples of “sweet” to “bitter” cassava food products in Camaroon was reported to range from 18.6 to 94.9 mg/kg hydrogen cyanide (17.9-91.4 $\mu\text{g CN}^-$) d/w for a dried cassava flour, and from 0.0 to 0.9 mg/kg hydrogen cyanide (0.0-0.9 $\mu\text{g/g CN}^-$) d/w for a cassava paste (O’Brien et al. 1992). Improper processing of cassava roots may result in maintenance of cyanogenic content of cassava food products at levels which are toxic (Mlingi et al. 1992, 1993; O’Brien et al. 1992). Cassava is a starch staple, but it is low in protein (Gomez et al. 1988). Low protein intake results in a decrease in available sulfur for conversion of cyanide to thiocyanate (Mlingi et al. 1993; Tylleskar et al. 1992). Hydrogen cyanide concentrations in sorghum leaves have been reported to range from approximately 200-1,300 ppm (192-1,250 $\mu\text{g/g CN}^-$) wet weight (w/w), with higher concentrations observed in early growth stages and at lower levels of phosphorus fertilization (Chand et al. 1992).

In apricot pits, the cyanide concentration may vary from 8.9 to 217 mg/100 g (89-2,170 $\mu\text{g/g}$) w/w, depending on the type of cultivar, season, and geographic area (Lasch and El Shawa 1981). Swain et al. (1992) reported a mean cyanide concentration in black cherry (*Prunus serotina Ehrh.*) fruits somewhat greater than 3 $\mu\text{mol/seed}$ at maturity, which is equivalent to a mean cyanide content of 78 $\mu\text{g/seed}$; insufficient information was provided to allow conversion of these results to weight per weight (w:w) units. In a recent laboratory study, Voldrich and Kyzlink (1992) reported *cyanide concentrations in* canned unpitted fruits (peaches, apricots, plums, and cherries) ranging from 0 to 4 mg/kg $\mu\text{g/g}$ w/w, depending on the glycoside content of the raw fruits and the conditions of heat processing. These authors noted that the observed cyanide levels were not negligible relative to an allowable daily intake (ADI) value for cyanide of 0.05 mg/kg body weight. An adult (70 kg body weight) could consume approximately 1 kg of canned fruits with a cyanide content of 4 mg/kg without exceeding this ADI value; however, a safe portion for a child (15 kg body weight) would be only about 180 grams. The analysis of 233 samples of commercially available and homemade stone-fruit juices showed that pitted fruit juices had lower cyanide concentrations than unpitted or partially pitted fruit juices, indicating that the pits are the primary sources of cyanides in these juices (Stadelmann 1976). For example, the hydrogen cyanide content of a home-made mixed cherry juice from pitted fruits was 5.3 mg/L, compared to 23.5 mg/L in a cherry juice containing 100% crushed pits. This study also reported the following levels (median concentrations in mg/L) of hydrogen cyanide in commercial fruit juices: cherry, 4.6; apricot, 2.2; prune, 1.9; and peach, 2.9. Stadelmann (1976) recommended that the maximum hydrogen cyanide content allowed in fruit juices should be set at a level of 5 mg/L.

5. POTENTIAL FOR HUMAN EXPOSURE

Cyanide can also be present in foodstuffs as residues from cyanide fumigation (Fiksel et al. 1981). Human exposure to naturally occurring cyanide in foods in the United States is expected to be low compared to certain populations in the Third World who subsist on cassava and similar crops (Fiksel et al. 1981).

Edible plants such as kale, cabbage, radishes, broccoli, brussels sprouts, cauliflower, collards, mustard greens, turnips, and kohlrabi contain glucosinolates which are hydrolysed by the endogenous enzyme myrosinase to produce toxic products, including thiocyanate (Abukutsa et al. 1993; Bible and Chong 1975; Bible et al. 1980; Carlson et al. 1985, 1987; Olea and Parras 1992; Olea-Serano et al. 1988). Vegetables from the Brassica family (e.g., cabbages, kohlrabi, kale) contain high levels of thiocyanate ranging from 5 to 660 $\mu\text{g/g}$ w/w (Weuffen et al. 1984). Kale leaves have been reported to contain concentrations of potassium thiocyanate at harvest ranging from 447 to 5,067 ppm $\mu\text{g/g}$ d/w (equivalent to thiocyanate concentration of 267-3,035 $\mu\text{g/g}$ d/w) depending on the fertilizer nitrogen source (Abukutsa et al. 1993). Other commonly consumed vegetables (e.g., lettuce, spinach, radishes) have been found to contain thiocyanate at concentrations ranging from approximately 0.1-5.0 $\mu\text{g/g}$ w/w, with concentrations usually <2.0 $\mu\text{g/g}$ w/w (Weuffen et al. 1984). Milk and other dairy products have been reported to contain thiocyanate at concentrations ranging from cl to 9.0 $\mu\text{g/g}$; whereas concentrations in meat products have been reported to range from only 0.5 to 0.7 $\mu\text{g/g}$ (Weuffen et al. 1984).

Laetrile (amygdalin), a drug formerly used in clinical trials for the treatment of cancer (Khandekar and Edelman 1979); sodium nitroprusside, a drug used to reduce high blood pressure (Aitken et al. 1977; Vesey et al. 1976); and a series of commercially important, simple, aliphatic nitriles (e.g., acetonitrile, propionitrile, acrylonitrile, n-butyronitrile, maleonitrile, succinonitrile) (Willhite and Smith 1981) release cyanide upon metabolism. These drugs and industrial chemicals have been associated with human exposure to cyanide and have caused serious poisoning and, in some cases, death.

Reported levels of cyanide in tobacco smoke are quite variable. Cyanide levels in mainstream (inhaled) smoke from U.S. commercial cigarettes have been reported to range from 10 to 400 μg per cigarette, with the ratio of cyanide concentration in sidestream smoke to mainstream smoke ranging from 0.006 to 0.27 (Fiksel et al. 1981). In studies which have included non-U.S. commercial cigarettes, hydrogen cyanide concentrations in mainstream and sidestream smoke ranging from 280 to 550 $\mu\text{g/cigarette}$ and 53 to 111 $\mu\text{g/cigarette}$, respectively, have been reported; sidestream/mainstream ratios of hydrogen cyanide concentrations ranged from 0.06 to 0.50 (Baker and Proctor 1990; Guerin et al. 1987).

5. POTENTIAL FOR HUMAN EXPOSURE

Cyanides have been detected in automobile exhaust. The average emission rate was 11-14 mg/mile for cars not equipped with catalytic converters and 1 mg/mile for cars with catalytic converters operating under optimum conditions. Cars with malfunctioning catalytic converters may emit as much or more hydrogen cyanide than cars without such equipment (Fiksel et al. 1981).

5.5 GENERAL POPULATION AND OCCUPATIONAL EXPOSURE

The general population may be exposed to cyanide from inhaling air and ingesting food and drinking water contaminated with it. Since most of the cyanide in the air will be present as hydrogen cyanide (see Section 5.3.2.1), the primary inhalation exposure to cyanide will occur from hydrogen cyanide. The concentration of hydrogen cyanide in the air of non-urban areas is \approx 160-166 ppt (see Section 5.4.1). Based on an atmospheric hydrogen cyanide concentration of 170 ppt (188 ng/m^3) and an average daily inhalation volume of 20 m^3 , the inhalation exposure of the general U.S. non-urban, nonsmoking population to hydrogen cyanide is estimated to be $3.8 \text{ } \mu\text{g/day}$. In drinking water, cyanide may be present as cyanogen chloride (see Section 5.4.2). In 1988, the quarterly median cyanogen chloride concentration in drinking water from 35 U.S. water utilities ranged from 0.45 to $0.8 \text{ } \mu\text{g/L}$ (0.19 to $0.3 \text{ } \mu\text{g/L}$ cyanide) (Krasner et al. 1989). Based on a daily drinking water consumption of 2 L for a 70-kg adult, the daily intake of cyanogen chloride is estimated to be 0.9 - $1.6 \text{ } \mu\text{g}$, which is equivalent to 0.4 - $0.7 \text{ } \mu\text{g}$ of hydrogen cyanide. EPA has established a maximum concentration level (MCL) of 0.2 mg/L for cyanide in drinking water (see Chapter 7), which is equivalent to a daily intake of 0.4 mg , based on a daily drinking water consumption rate of 2 L for a 70-kg adult (EPA 1991a). Estimates of the cyanide concentration in the total diet of a U.S. adult were not located in the available literature. Therefore, no estimate of daily cyanide intake from food can be made. In the United States, human exposure to cyanide from foods in which it occurs naturally is expected to be low, but is likely to exceed cyanide intake from inhalation of air and ingestion of drinking water (Fiksel et al. 1981). The EPA has established tolerances for hydrogen cyanide and calcium cyanide in various foods ranging from 25 to 250 ppm (EPA 1971b, 1971c, 1975b) and from 5 to 25 ppm (EPA 1971a), respectively (see Chapter 7). Poitras et al. (1988) have estimated an overall allowable daily intake of 0.6 mg for cyanide, incorporating a safety factor of 100-1,000 to ensure that the potential for an infant receiving a toxic dose of cyanide from breast milk is quite low.

The dietary cyanide intake of Tukanoan Indians in northwest Amazonia who rely heavily on high (>70% of all foods) cyanide-containing varieties of cassava was estimated to be $>20 \text{ mg/day}$ (Dufour 1988). The cassava processing techniques of the Tukanoans are very sophisticated and very effective in reducing the cyanide concentration in the crop. The author did not find physical disorders in Tukanoan Indians

5. POTENTIAL FOR HUMAN EXPOSURE

attributable to high cassava diets, in contrast to observations about cassava-consuming populations in Africa. Also, the variety of cassava may differ between geographical areas, which may account for the observed differences in toxicity among different populations (Rosling 1988). However, in some African populations, outbreaks of acute cyanide intoxications have been found to result from incomplete processing of cassava, resulting in highly elevated cyanide levels in combination with chronic dietary protein malnutrition. This occurred when, due to a food shortage, the lengthy sun drying normally used to remove cyanogenic glucosides was replaced by repeated pounding and drying to obtain flour for consumption in one day (Mlingi et al. 1992, 1993; Tylleskar et al. 1992).

The primary route of exposure to thiocyanates for the general population appears to be from ingestion of foods in which thiocyanate occurs naturally (e.g., cabbage, kale, spinach, kohlrabi). Estimates of the thiocyanate concentration in the total diet of an adult in the United States were not located in the available literature; however, these would be expected to be quite low. Exposure to cyanide also is a source of thiocyanate exposure because thiocyanate is a major metabolite of cyanide in the human body.

Occupational exposures to cyanide are expected to occur primarily through inhalation and, less frequently, through skin absorption. Preliminary data from the NOES conducted by NIOSH from 1980-83 estimated that the number of workers potentially exposed to cyanide compounds in the United States from 1981 to 1983 are as follows (NIOSH 1989a): cyanide, 367; hydrogen cyanide, 4,005; sodium cyanide, 66,493; potassium cyanide, 64,244; potassium silver cyanide, 3,215; calcium cyanide, 3,606; copper(I) cyanide, 22,339; ammonium thiocyanate, 90,599; cyanogen chloride, 1,393. Thiocyanate and cyanogen were not included in the NOES (NIOSH 1989a). These numbers do not include workers potentially exposed to trade-name compounds that contain cyanides or thiocyanates. Workers in various occupations may be exposed to cyanide compounds. People possibly exposed to cyanide include workers involved in electroplating, metallurgy, cyanotype printing, pesticide application, firefighting, steel manufacturing, and gas works operations; workers involved in the manufacture of cyanides, adiponitrile and other simple, aliphatic nitriles, methyl methacrylate, cyanuric acid, dyes, pharmaceuticals, or chelating agents; and people who work in tanneries, blacksmithing, metal cleaning, and photoengraving or photography industries (Fiksel et al. 1981; Lucas 1992; Willhite and Smith 1981). Workers in the oil shale retorting industry may be exposed to cyanide because the offgas from the retorting process contains hydrogen cyanide (see Section 5.2.1). Medical and emergency personnel (e.g., police and firefighters) who may be involved in resuscitation efforts or removal of gastric contents of postmortem victims of cyanide poisoning are potentially exposed to higher levels of cyanide (Andrews et al. 1989). The manufacture of industrial inorganic chemicals may be a significant potential source of occupational exposure to cyanogen

5. POTENTIAL FOR HUMAN EXPOSURE

chloride (NIOSH 1989a). Potential sources of occupational exposure to ammonium thiocyanate include the manufacture of electronic computing equipment, research and development laboratories, newspaper and other commercial printing, general medical and surgical hospitals, production of adhesives and sealants, and the construction and furniture industries (NIOSH 1989a).

In a survey of the plating facility of a national airline conducted by NIOSH in December 1981, the concentrations of hydrogen cyanide in 3 work areas ranged from 0.001 to 0.004 mg/m³ (0.0009 to 0.004 ppm) (NIOSH 1982). The cyanide concentrations in 4 work areas in a plating facility of an electrical and electronic company in Waynesboro, Virginia, ranged from 0.07 mg/m³ (0.07 ppm hydrogen cyanide) in a salt pot room to 4.3 mg/m³ (4.0 ppm hydrogen cyanide) beside a stripping tank (NIOSH 1976). Similarly, the concentration of cyanide in the breathing zone air of workers in a plating facility in Galion, Ohio, was 1.7 mg/m³ (1.6 ppm hydrogen cyanide) (NIOSH 1978). In a recent NIOSH survey of a university art department foundry, hydrogen cyanide was detected in the smoke produced during pouring and knockout of castings at a concentration of approximately 4 ppm; hydrogen cyanide was not detected in personal breathing zone samples taken during knockout of castings (Lucas and Salisbury 1992). These levels are all below the NIOSH recommended ceiling limit of 4.7 ppm (NIOSH 1992).

Levels of cyanide and its metabolite thiocyanate in blood serum and plasma, urine, and saliva have been used as indicators of cyanide exposure in humans, particularly in workers at risk of occupational exposures, in smokers or nonsmokers exposed to sidestream or environmental tobacco smoke, in populations exposed to high dietary levels of cyanide, and in other populations with potentially high exposures (see Section 5.6). The correlation between increased cyanide exposure and urinary thiocyanate levels was demonstrated in workers exposed to 6.4-10.3 ppm cyanide in air (El Ghawabi et al. 1975). In another study, blood cyanide concentrations were found to vary from 0.54 to 28.4 µg/100 mL in workers exposed to approximately 0.2-0.8 ppm cyanide in air, and from 0.0 to 14.0 µg/100 mL in control workers (Chandra et al. 1988). Similar elevations in urinary thiocyanate levels were observed, with concentrations for exposed workers and controls ranging from 0.05 to 2.80 and 0.02 to 0.88 mg/mL, respectively.

The results of several studies which have shown elevated cyanide or thiocyanate concentrations in body fluids of smokers are summarized in Table 5-3. In general, these results indicate that serum cyanide levels (Cardeal et al. 1993; Symington et al. 1987) and plasma, serum, and saliva thiocyanate levels (Banerjee and Muthu 1994; Jarvis 1989; Maliszewski and Bass 1955; Pre and Vassy 1992, 1993; Waage et al. 1992; Yamanaka et al. 1991) could distinguish smokers from nonsmokers and/or light smokers. Pre and Vassy (1992) found that plasma thiocyanate was an indicator of smoking status that was not sensitive to light or

Table 5-3. Cyanide and Thiocyanate Concentrations ($\mu\text{g/mL}$)^a in Smokers and Nonsmokers

Compound	Plasma		Serum		Saliva		Urine		Reference
	S ^b	NS ^b	S	NS	S	NS	S	NS	
Cyanide									
			2.11 (1.42–3.67)	0.78 (0.44–1.15)					Cardeal et al. 1993 ^c
			6.8 (1.3–19.4)	2.9 (0.0–11.7)					Symington et al. 1987 ^{c,d}
Thiocyanate									
			232 (10)	92 (9)					Banerjee and Muthu 1994 ^e
	7.1 7.1 (6.2–8.6)	2.9 2.0 (1.2–2.8)			142 75.7 (48.4–112.2)	76 20.3 (9.71–28.7)	9.0 12.3 (7.8–17.2)	5.8 2.1 (1.1–3.9)	Jarvis 1989 ^f Maliszewski and Bass 1955 ^c
	8.7 ^g (4.4–21.5)	1.8 ^h (0.5–4.4)							Pré and Vassy 1992 ^e
	3.3 ⁱ (1.0–4.6)								
			6.6 (1.5)	1.2 (0.3)					Pré and Vassy 1993 ^e
			(<0.05–0.35)	(<0.05–0.08)					Waage et al. 1992 ^{e,j}
	2.1	3.7			88	33	18	19	Yamanaka et al. 1991 ^{j,k}

^a Values are means; values in parentheses are ranges or standard deviations.

^b S = smoker; NS = nonsmoker

^c No statistics reported

^d As cited in Cardeal et al. 1993

^e Results significantly different

^f Results not significantly different

^g Inhaling smokers

^h Nonsmokers including passive smokers

ⁱ Noninhaling smokers

^j Values estimated from graphical presentation of data

^k All results, except urine, significantly different

5. POTENTIAL FOR HUMAN EXPOSURE

passive smoking. However, inhaling smokers were easily distinguished from noninhaling smokers. The authors concluded that a plasma thiocyanate concentration below 20 $\mu\text{mol/L}$ (1,200 $\mu\text{g/L}$) indicated that passive smoking was very unlikely; whereas concentrations above 80-85 $\mu\text{mol/L}$ (4,600-4,900 $\mu\text{g/L}$) were a reliable indication of active inhaling smoking. Yamanaka et al. (1991) found a correlation between the number of cigarettes smoked per day and the thiocyanate levels in plasma and saliva; however, in apparent contrast to results obtained by Maliszewski and Bass (1955), thiocyanate concentrations in urine of smokers and nonsmokers were not found to be significantly different. Chen et al. (1990) found that serum thiocyanate concentrations of 1 %month-old infants heavily exposed to environmental tobacco smoke (>20 cigarettes a day smoked in the home) were significantly higher than those of unexposed infants ($p < 0.05$). Mean concentrations (\pm SD) in these respective groups were $36.2 \pm 14.88 \mu\text{mol/L}$ (2.1 f 0.9 $\mu\text{g/mL}$) and $27.7 \pm 10.7 \mu\text{mol/L}$ ($1.6 \pm 0.6 \mu\text{g/mL}$).

Positive correlations between fetal umbilical serum thiocyanate levels and serum thiocyanate levels of smoking mothers (Bottoms et al. 1982; Hauth et al. 1984) and mothers exposed to environmental tobacco smoke in the home (Bottoms et al. 1982) have been reported. Hauth et al. (1984) found that the mean serum thiocyanate concentration (95 $\mu\text{mol/L}$; 5.5 $\mu\text{g/mL}$) was significantly higher ($p < 0.001$) in smokers than in passive smokers (35.9 $\mu\text{mol/L}$; 2.1 $\mu\text{g/mL}$) or nonsmokers (32.3 $\mu\text{mol/L}$; 1.9 $\mu\text{g/mL}$). Similarly, the mean umbilical thiocyanate concentration in the newborn infants of smoking mothers (72 $\mu\text{mol/L}$; 4.8 $\mu\text{g/mL}$) was significantly higher than those in newborn infants of passive smokers (26 $\mu\text{mol/L}$; 1.5 $\mu\text{g/mL}$) and nonsmokers (23 $\mu\text{mol/L}$; 1.3 $\mu\text{g/mL}$). In contrast, Bottoms et al. (1982) found that among newborn infants of nonsmoking mothers, fetal umbilical thiocyanate concentrations increased with passive smoking in the home ($p < 0.05$).

Data on elevated levels of thiocyanate in body fluids resulting from consumption of cyanide-containing foods come primarily from populations in tropical regions which may consume large quantities of improperly processed cyanogenic plants such as cassava. Among four populations in Africa known to be exposed to high levels of dietary cyanide because of incomplete processing of cassava during drought periods, urinary thiocyanate concentrations (mean f SE) ranged from 350 f 39 to 1,120 f 75 $\mu\text{mol/L}$ (20 ± 2 - $65 \pm 4 \text{ mg/L}$), compared to urinary thiocyanate levels in the normal population of less than 100 $\mu\text{mol/L}$ (5.8 $\mu\text{g/L}$) (Mlingi et al. 1992, 1993; Tylleskar et al. 1992). The mean plasma thiocyanate concentration in one of these populations was $335 \pm 12 \mu\text{mol/L}$ ($19 \pm 1 \mu\text{g/L}$), compared to 28 f 4 $\mu\text{mol/L}$ ($1.6 \pm 0.2 \mu\text{g/L}$) in a control population (Mlingi et al. 1992). Elevated mean serum thiocyanate concentrations ($11 \pm 3 \mu\text{g/L}$) compared to reference values of 0.5-4 $\mu\text{g/L}$) were observed in only one of two populations in which this

5. POTENTIAL FOR HUMAN EXPOSURE

biomarker was measured (Tylleskar et al. 1992, 1994). There was no apparent explanation for this difference.

High serum thiocyanate concentrations (>180 pmol/L) have been found in Tukanoan Indians on traditional diets. However, the levels of residual cyanide appear to be tolerated well (Dufour 1988).

5.6 POPULATIONS WITH POTENTIALLY HIGH EXPOSURES

Among the general population, subpopulations with the most likely potential for exposure to cyanide and thiocyanate include active and passive smokers (Fiksel et al. 1981) and people who are exposed to house or other building fires (Andrews et al. 1989). Other subpopulations with potentially high cyanide or thiocyanate exposures are residents who live near industrial sites releasing cyanides or thiocyanates into the environment, residents who live near cyanide- or thiocyanate-containing hazardous waste sites, and people who consume foods high in cyanogenic glycosides. The fetuses of pregnant women who smoke or who are exposed to high levels of environmental smoke (i.e., passive smokers) may be subjected to potentially high exposures of cyanide and thiocyanate (Bottoms et al. 1982; EPA 1992f; Hauth et al. 1984). Workers involved in electroplating, metallurgy, pesticide application, firefighting, gas works operations, tanning, blacksmithing, metal cleaning, photoengraving, photography, cyanotype printing, the manufacture of steel, cyanides, adiponitrile and other nitriles, methyl methacrylate, cyanuric acid, dyes, pharmaceuticals, or chelating agents have the potential to be occupationally exposed to higher concentrations of cyanide than the general population (Fiksel et al. 1981; NIOSH 1989a). Workers in the following industries may also be exposed to higher concentrations of thiocyanate than the general population: manufacture of electronic computing equipment, research and development laboratories, newspaper and other commercial printing, general medical or surgical hospitals, production of adhesives and sealants, pesticide application, building and furniture construction, and handling, treatment or disposal of thiocyanate-containing wastes from industrial processes (Brown and Morra 1993; NIOSH 1989a). Two additional groups of people who may be at greater risk for cyanide exposure are those who are exposed to cyanide but are unable to smell the chemical (EPA 1987a) and patients with motor neuron disease (see Section 2.7).

Data related to the levels of cyanide or thiocyanate exposure in several of these population groups have been presented in Section 5.5. No data were found related to the levels of cyanide or thiocyanate exposure in cassava eaters in the United States. Also, no data were located in the available literature related to the levels of cyanide and thiocyanate exposure of people who live near industrial sites releasing cyanides or

5. POTENTIAL FOR HUMAN EXPOSURE

thiocyanates to the environment, or near hazardous waste sites. Cyanides (reported as cyanide, hydrogen cyanide, sodium cyanide, potassium cyanide, calcium cyanide, or copper (I) cyanide) have been detected in air, surface and groundwater, and soil samples at NPL hazardous waste sites; cyanogen and cyanogen chloride have been detected in soil samples at NPL hazardous waste sites; and thiocyanates have been detected in surface and groundwater, and soil samples at NPL sites (see Section 5.2) (HazDat 1996). There is a need for reliable data on the levels at which these substances are found in various media at these sites in order to estimate potential exposures of people living near hazardous waste sites.

5.7 ADEQUACY OF THE DATABASE

Section 104(i)(5) of CERCLA, as amended, directs the Administrator of ATSDR (in consultation with the Administrator of EPA and agencies and programs of the Public Health Service) to assess whether adequate information on the health effects of cyanide is available. Where adequate information is not available, ATSDR, in conjunction with NTP, is required to assure the initiation of a program of research designed to determine the health effects (and techniques for developing methods to determine such health effects) of cyanide.

The following categories of possible data needs have been identified by a joint team of scientists from ATSDR, NTP, and EPA. They are defined as substance-specific informational needs that if met would reduce or eliminate the uncertainties of human health assessment. This definition should not be interpreted to mean that all data needs discussed in this section must be filled. In the future, the identified data needs will be evaluated and prioritized, and a substance-specific research agenda will be proposed.

5.7.1 Identification of Data Needs

Physical and Chemical Properties. As reported in Section 3.2, the relevant physical and chemical properties of cyanide compounds are known. Certain physical parameters such as octanol/water partition coefficient and soil partition coefficient that are used generally for covalently bound organic compounds to predict environmental fate and transport are neither available nor useful for most of the ionic cyanide compounds.

Production, Import/Export, Use, Release, and Disposal. Knowledge of a chemical's production volume is important because it may indicate the magnitude of environmental contamination and human exposure. Data regarding the production, trend, use pattern, and disposal of commercially significant

5. POTENTIAL FOR HUMAN EXPOSURE

cyanide compounds are available (CMR 1993; Curry 1992; Homan 1987; HSDB 1996; Sittig 1980; SRI 1994; TRI93 1995). It is known that the import and export of hydrogen cyanide is insignificant compared to its production; however, except for potassium cyanide, recent import and export data for other individual cyanide compounds are difficult to obtain (USDOC 1994). There are some less recent data regarding the release of cyanides in air (Fiksel et al. 1981; TRI88 1990) but, except for hydrogen cyanide (TRI93 1995), more recent quantitative data regarding the release of cyanide compounds in air, water, and particularly soil and sediment are unavailable.

According to the Emergency Planning and Community Right-to-Know Act of 1986, 42 U.S.C. Section 11023, industries are required to submit chemical release and off-site transfer information to the EPA. The Toxics Release Inventory (TRI), which contains this information for 1992, became available in May of 1994. This database will be updated yearly and should provide a list of industrial production facilities and emissions. Information in the TRI93 (1995) data base pertains only to U.S. industrial facilities that manufacture or process hydrogen cyanide. There is a need for similar information on releases and off-site transfer from facilities that manufacture or process other cyanide compounds covered in this profile.

Cyanide is naturally present in many foods high in cyanogenic glycosides (Fiksel et al. 1981; Honig et al. 1983; Towill et al. 1978). No information was located in the available literature to indicate that cyanide enters foods during processing or that elevated cyanide concentrations are present in any consumer products. The two most likely sources of general population exposure to cyanide include people who inhale cigarette smoke (Fiksel et al. 1981) or individuals who are exposed to a house or other type of building fire (Andrews et al. 1989). There are EPA regulations regarding the disposal of cyanide wastes and OSHA and NIOSH regulations regarding the levels of hydrogen cyanide in workplaces (see Chapter 7). Additional research is needed on improved methods of pollution prevention and biodegradation to reduce or eliminate releases of cyanide compounds to the environment from industrial processes.

Environmental Fate. The environmental fate of hydrogen cyanide gas in air is well studied (Cicerone and Zellner 1983; Fritz et al. 1982); however, it would be useful if the role of particulate cyanides (e.g., sodium cyanide, potassium cyanide) in determining the fate of total cyanides in the air was known. Given that hydrogen cyanide occurs in the atmosphere from both natural and anthropogenic processes (Cicerone and Zellner 1983; Crutzen and Andreae 1990; Crutzen and Carmichael 1993; Fiksel et al. 1981; Knowles 1988; Lobert and Warnatz 1993), it would be useful if an estimate were available for the contribution of anthropogenic processes to the overall hydrogen cyanide burden in the atmosphere. It is generally known that volatilization and biodegradation will be important processes for the loss of cyanides in water

5. POTENTIAL FOR HUMAN EXPOSURE

(Callahan et al. 1979; Ludzack et al. 1951; Raef et al. 1977a; Towill et al. 1978), but no experimental or estimated values for the half-life of cyanides in ambient water are available. No comprehensive data regarding the role of sorption in determining the fate of cyanides in water are available. It is generally known that volatilization from soil surfaces and biodegradation play significant roles in the loss of cyanides in soil (Towill et al. 1978), but no quantitative data regarding the half-life of cyanides in ambient soil are available. Additional data on the relative importance of volatilization and biodegradation in determining the fate of cyanides in soils are needed. The elucidation of the role of cyanide complexation by metals in soil and sediment in controlling the fate of cyanide would be useful.

Both cyanogen and cyanogen chloride are highly volatile gases, indicating that volatilization would be the major transport pathway for these compounds from surface water and soils. Cyanogen is highly reactive and does not persist in the environment unchanged (Towill et al. 1978). It also has been reported to react slowly with water to yield hydrogen cyanide and cyanic acid, among other products (Callahan et al. 1979), and this hydrolysis reaction may be a possible degradation pathway. Additional information on the environmental fate of cyanogen and cyanogen chloride is needed.

There is almost no available information on the environmental transport and partitioning of thiocyanate in the environment. At ambient temperatures, it appears that sorption and volatilization are not significant partitioning processes for thiocyanate in soil, with thiocyanate losses due primarily to microbial degradation (Brown and Morra 1993); however, additional research is needed in this area. Although biodegradation is a significant transformation process for thiocyanate in water, additional data are needed on the relative importance of this process in determining the fate of thiocyanates in natural water systems.

Bioavailability. Cyanide is known to be absorbed following inhalation, oral, and dermal contact (Gosselin et al. 1976; Rieders 1971). The environmental factors that may influence the bioavailability of cyanide from contaminated air, water, soil, or plant material have not been studied. Since cyanides are not strongly sorbed to soil and sediments (Callahan et al. 1979), the role of sorption may not be significant in determining the bioavailability of cyanides from different soils or waters. The bioavailability of cyanide from an environmental medium is expected to increase if the cyanide is present in water-soluble forms, such as ions or soluble complexes. The pH of a medium may also be significant in determining the bioavailability because hydrogen cyanide gas may be released as the pH of the medium decreases (Callahan et al. 1979; Towill et al. 1978). Data delineating the factors affecting the bioavailability of cyanide compounds from soil and other environmental media need further development, since the absorption studies discussed in Section 2.3.1 have been performed with the pure chemical.

5. POTENTIAL FOR HUMAN EXPOSURE

The factors that may influence the bioavailability of thiocyanate from various foods and other environmental media have not been investigated.

Food Chain Bioaccumulation. Simple cyanide compounds do not bioconcentrate in fish (ASTER 1994; Callahan et al. 1979; EPA 1985a). It would be useful to determine the bioconcentration potential for cyanide in fish from water dosed with less toxic and water-soluble cyanide complexes. There is no indication of biomagnification of cyanides in aquatic and terrestrial food chains. Because of the high toxicity of cyanides at high doses and rapid metabolism at low doses, biomagnification of cyanide in animals seems unlikely.

No information could be found in the available literature on the potential of thiocyanates for bioconcentration and food chain bioaccumulation.

Exposure Levels in Environmental Media. Data regarding the cyanide and thiocyanate levels in ambient air and drinking water are lacking; therefore, it is not possible to estimate exposure levels to cyanides from inhaling ambient air and ingesting drinking water. Although the cyanide and thiocyanate concentrations in certain foods are known (Abukutsa et al. 1993; Fiksel et al. 1981; Honig et al. 1983; Pre and Vassy 1992; Towill et al. 1978), neither the cyanide nor the thiocyanate content of a total diet sample consumed by an average adult is known; therefore, the dietary exposures of an average person to cyanide and thiocyanate are unknown. Reliable monitoring data for the levels of cyanide and thiocyanate in air, water, and total diet samples would be useful in estimating exposures from each source. Additional data on the levels of cyanide and thiocyanate in soils will also be useful. It will also be useful to develop data that would clearly establish whether cyanides or thiocyanates pose acute or chronic exposure hazards for residents in the vicinity of hazardous waste sites. This information should include data on background concentrations in all media.

Reliable monitoring data for the levels of cyanide and thiocyanate in contaminated media at hazardous waste sites are needed so that the information obtained on levels of cyanide and thiocyanate in the environment can be used in combination with the known body burdens of cyanide and thiocyanate to assess the potential risk of adverse health effects in populations living in the vicinity of hazardous waste sites. Also, there is a need for data relating to exposure levels of cassava eaters in the United States.

Exposure Levels in Humans. The levels of cyanide and thiocyanate in various human tissues and body fluids of both control and occupationally exposed groups and of smokers and nonsmokers are

5. POTENTIAL FOR HUMAN EXPOSURE

available (see Sections 2.3.4, 2.6.1, and 5.5). The levels of these chemicals in humans consuming foods containing cyanogenic materials also are available.

Exposure Registries. No exposure registries for cyanide or thiocyanate were located. These compounds are not currently among the compounds for which a subregistry has been established in the National Exposure Registry. These compounds will be considered in the future when chemical selection is made for subregistries to be established. The information that is amassed in the National Exposure Registry facilitates the epidemiological research needed to assess adverse health outcomes that may be related to exposures to these compounds.

5.7.2 Ongoing Studies

A search of the Federal Research in Progress database (FEDRIP 1994) indicates that the following research studies are in progress to fill in the data gaps discussed in Section 5.7.1.

The U.S. Bureau of Mines-Reno Research Center is conducting studies on the use of thiosulfate as an alternative to cyanide for refractory gold ores as a means of pollution prevention and on the fate of cyanide in solution after land application.

The U.S. Bureau of Mines-Twin Cities Research Center is conducting research on the development of novel hydrological and geochemical systems for in situ leach mining which includes development of a new noncyanic, nontoxic precious metals lixiviant which is a good candidate for in situ mining systems where groundwater contamination is of paramount concern.

The Department of Federal Affairs, Washington, D.C., is evaluating the use of gamma radiation as an energy source for the photolytic destruction of aqueous organic wastes, including cyanide.

The U.S. EPA is funding research at Ionedge Corporation, Fort Collins, Colorado, to develop a process for zinc-graphite and zinc-cadmium alloy dry plating as environmentally safer alternatives to cadmium electroplating in cyanide baths. Successful development of these technique could lead to a method which would potentially eliminate the environmental and occupational hazards associated with cadmium electroplating.

5. POTENTIAL FOR HUMAN EXPOSURE

The U.S. EPA is funding research at Emec Consultants, Export, Pennsylvania, on methods to suppress or eliminate cyanide formation in spent potlining from industrial primary aluminum production cells. Because over 100,000 tons of this material are disposed in landfills annually, it would be desirable to avoid the formation of cyanide during the production of the cells.

The European Coal and Steel Community is funding research at Stoke Orchard, Cheltenham, Gloucestershire, to develop a catalyst for the conversion of ammonia and hydrogen cyanide in coal gasification and combustion gases to nitrogen at high temperatures. Successful completion of this research will provide methodology to eliminate release of hydrogen cyanide to the atmosphere from these processes.

The CSIRO Division of Mineral Products, Port Melbourne, Victoria, Australia, is conducting research to develop a process to recover fluoride and aluminum from spent pot lining ash with concurrent production of an environmentally safe residue that is suitable for disposal. The proposed method involves initial calcination which thermally decomposes the cyanide in the spent pot lining. Successful completion of this research would reduce the amount of hazardous wastes that contain potentially harmful leachable cyanides that can enter the groundwater during open air storage.

The National Science Foundation is funding research at the South Dakota School of Mines, Rapid City, South Dakota, to develop an alternative approach to the extraction of precious metals from refractory ores which will pose a much lesser threat to environmental quality than the presently predominant cyanide leaching process.

The U.S. Department of Energy is funding research at Allied-Signal, Inc., Kansas City, Missouri, which involves integrating advanced pollution prevention and waste minimization technologies into U.S. industry. One major area of technology integration is plating replacements for cyanide, hexavalent chromium, cadmium-containing compounds, and other heavy metals.

The U.S. Department of Energy is funding research at the Idaho National Engineering Laboratory, Idaho Falls, Idaho, to determine if sawdust can be used exclusively to support a bioprocess for the remediation of acid mine drainage containing significant concentrations of cyanide and other ions.

5. POTENTIAL FOR HUMAN EXPOSURE

The U.S. Bureau of Mines-Reno Research Center is conducting research on the chemical treatment of process waste waters by ion elutriation for removing low levels of anions from cyanide solutions. This research has been coordinated with other centers for developing a waste water treatment system.

The U.S. Bureau of Mines-Salt Lake Research Center is conducting research to develop new biohydrometallurgical techniques to decontaminate mining and milling wastes containing heavy metals and toxic chemicals. Bacterial techniques are being developed to remove cyanide and selenium from waste water.

The Bureau of Mines-Reno Research Center is conducting research to identify and quantify noxious metals and compounds, including cyanide, that must be removed from leaching wastes and to develop a technology to be applied during closure to render leaching wastes compatible with the environment. This research has involved developing closure data and rinsing techniques for leaching operations and conducting field studies to identify compounds and species in leaching wastes.

The National Institute of General Medical Sciences is funding research at Selma University, Selma, Alabama, on the biodegradation of sodium cyanide in a fixed reactor.

The German Ministry for Research and Technology is funding research at the Bergbau-Forschung GmbH, Research Institute of the Coal Mining Society, Essen, Germany, on biological treatments of effluents from coal upgrading plants. Special cultures will be developed to improve the biological purification performance, particularly with regard to the degradation of xenobiotics, cyanide and rhodanide.

The National Institute of Environmental Health Sciences is funding research at the University of Nevada at Reno on the chemical environmental problems associated with mining of gold and silver in the desert environment of the western United States. Cyanide will be the focus of an environmental chemistry project which is intended to provide essential site and chemical characterization information to concurrent biomedical projects. This research will provide information on releases of cyanide to the environment from precious metal mining and help to determine the threat to human health (i.e., potential for human exposures to cyanide) from toxic mining waste.

The U.S. Bureau of Mines-Tuscaloosa Research Center is conducting research to determine the composition of cyanide leached gold tailings and identify the constituents leached from those tailings through laboratory and field studies. Results of this research should increase understanding of the

5. POTENTIAL FOR HUMAN EXPOSURE

environmental impact of untreated fine tailings generated from gold milling operations, especially in humid climates and should also provide useful information in evaluating the regulations promulgated by the U.S. EPA and the individual state regulatory agencies on the impoundment and abandonment of the tailings.

The U.S. Bureau of Mines-Spokane Research Center is conducting research on the environmental impacts of placing mine wastes underground as backfill. This work includes a review of residual cyanide in placed landfill, water quality monitorings at two mines and laboratory tests of cyanide fate in underground environments and permeability/leachate effects through cemented tailings.

The Maine Department of Transportation is funding research at Maine University, Orono, Maine, to monitor the levels of simple cyanide and complex cyanides, pH, Na, and Cl in surface waters which are in the proximity of four Maine Department of Transportation salt storage facilities.

The U.S. Department of the Interior is conducting research under the U.S. Geological Survey to determine the impacts of highway de-icing chemicals on the groundwater quality of shallow, unconsolidated aquifers in Ohio, and to determine the salt concentration present in the soil and unsaturated zones. This research will include some analyses for dissolved cyanide in monthly samples from eight sites across Ohio.